

DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

**TOPICAL REPORT: TEST RESULTS FOR A GAS-FIRED PROCESS HEATER (SITE
ALPHA)**



When citing this document, please use the following citation:

Wien, S., England, G.C. and Chang, O.M.C., “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for a Gas-Fired Process Heater (Site Alpha), 2003.”

DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

TOPICAL REPORT: TEST RESULTS FOR A GAS-FIRED PROCESS HEATER (SITE ALPHA)

Prepared by:

Stephanie Wien, Glenn C. England, and M.C. Oliver Chang
GE Energy and Environmental Research Corporation
18 Mason
Irvine, CA 92618

Prepared for:

National Petroleum Technology Office
National Energy Technology Laboratory
United States Department of Energy
(DOE Contract No. DE-FC26-00BC15327)

Gas Research Institute
California Energy Commission – Public Interest Energy Research (PIER)
New York State Energy Research and Development Authority
(GRI contract No. 8362)

American Petroleum Institute
(API Contract No. 00-0000-4303)

Draft (Revision 0): January 28, 2002
Draft (Revision 1): November 11, 2002
Final (Revision 2): May 6, 2003
Final (Revision 3, Version 3): January 30, 2004

LEGAL NOTICES

United States Department of Energy:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Gas Research Institute:

This report was prepared by GE Energy and Environmental Research Corporation (GE EER) as an account of contracted work sponsored by the Gas Research Institute (GRI). Neither GE EER, GRI, members of these companies, nor any person acting on their behalf:

- a. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any apparatus, methods, or process disclosed in this report may not infringe upon privately owned rights; or
- b. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

California Energy Commission:

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the State of California. The Commission, the State of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

New York State Energy Research and Development Authority:

This report was prepared by GE Energy and Environmental Research Corporation in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (NYSERDA). The opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it. Further, NYSERDA and the State of New York make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. NYSERDA, the State of New York, and the contractor make no representation that the

use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

American Petroleum Institute (API):

API publications necessarily address problems of a general nature. With respect to particular circumstances, local state and federal laws and regulations should be reviewed.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations under local, state, or federal laws. Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

GE Energy and Environmental Research Corporation

This report was prepared by GE Energy & Environmental Research Corporation (as part of GE Power Systems and GE, collectively hereinafter “EER”) as an account of sponsored work. EER, nor any of their employees, makes any warranty, express or implied or otherwise, or assumes any legal liability or responsibility of the accuracy, completeness, or usefulness of any information, apparatus, processes, systems, products, methodology or the like disclosed herein, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply an endorsement, recommendation, or favoring by EER. The views and opinions of the authors expressed herein do not necessarily state or reflect those of EER. This report has not been approved or disapproved, endorsed or otherwise certified by EER nor has EER passed upon the accuracy or adequacy of the information in this report.

ACKNOWLEDGEMENTS

The following people are recognized for their contributions of time and expertise during this study and in the preparation of this report:

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

PROJECT TEAM MEMBERS

Glenn England, Project Manager

Stephanie Wien, Project Engineer

Dr. Oliver M.C. Chang, Project Engineer

Prof. Judith Chow, Desert Research Institute

Prof. John Watson, Desert Research Institute

Prof. Barbara Zielinska, Desert Research Institute

Prof. Lynn Hildemann, Stanford University

Prof. Philip Hopke, Clarkson University

AD HOC COMMITTEE MEMBERS

Dr. Karl Loos, Shell Global Solutions

Prof. James Schauer, University of Wisconsin-Madison

Dr. Praveen Amar, NESCAUM

Thomas Logan, U.S. EPA

Ron Myers, U.S. EPA

Karen Magliano, California Air Resources Board

PROJECT SPONSORS

Kathy Stirling, U.S. Department of Energy

Marla Mueller, California Energy Commission

Dr. Paul Drayton, Gas Research Institute

Karin Ritter, American Petroleum Institute

Barry Liebowitz, New York State Energy Research and Development Authority

Janet Joseph, New York State Energy Research and Development Authority

FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source receptor and source apportionment analysis;
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source receptor and source apportionment analysis; and
- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

This report is part of a series of progress, topical and final reports presenting the findings of the program.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1.0 PROJECT DESCRIPTION.....	1-1
PROJECT OVERVIEW	1-1
PROJECT OBJECTIVES	1-2
Primary Objectives.....	1-2
TEST OVERVIEW.....	1-3
Source Level (In-Stack) Samples.....	1-3
Diluted Exhaust Gas Samples	1-4
Process Samples.....	1-6
KEY PERSONNEL	1-6
2.0 PROCESS DESCRIPTION	2-1
SAMPLING LOCATIONS	2-1
3.0 TEST PROCEDURES.....	3-1
STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT	3-1
O ₂ , CO ₂ , CO, NO _x	3-1
IN-STOCK METHOD TESTS	3-1
In-Stack Total Filterable PM, PM10 and PM2.5	3-5
Condensable Particulate Matter Mass and Chemical Analysis.....	3-7
DILUTION SAMPLER TESTS	3-9
PM2.5 Mass	3-11
Elements.....	3-11
Sulfate, Nitrate, Chloride and Ammonium	3-12
Organic and Elemental Carbon.....	3-13
Volatile Organic Compounds	3-14
Semivolatile Organic Compounds	3-15
Carbonyls (Aldehydes and Ketones)	3-15
Sulfur Dioxide.....	3-16
Ammonia.....	3-16
4.0 TEST RESULTS.....	4-1
PROCESS OPERATING CONDITIONS	4-1
PRELIMINARY TEST RESULTS	4-4
STACK GAS CONDITIONS AND FLOW RATE.....	4-4
IN-STOCK AND IMPINGER METHOD RESULTS	4-4
Particulate Mass	4-4
DILUTION SAMPLER RESULTS.....	4-8
Particulate Mass	4-8
Sulfate, Nitrate, Chloride, and Ammonium	4-10
OC, EC and Organic Species	4-11
Elements.....	4-16
Carbonyls (Aldehydes and Ketones)	4-16
Secondary Particle Precursors.....	4-21

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
5.0 EMISSION FACTORS AND SPECIATION PROFILES	5-1
UNCERTAINTY	5-1
EMISSION FACTORS.....	5-1
PM2.5 SPECIATION PROFILES.....	5-7
Dilution Sampler.....	5-7
Organic Aerosols	5-9
Method PRE-4/202	5-11
6.0 QUALITY ASSURANCE.....	6-1
SAMPLE STORAGE AND SHIPPING.....	6-1
DILUTION SAMPLER FLOWS	6-1
DILUTION SAMPLER QUALITY ASSURANCE SAMPLES	6-1
GRAVIMETRIC ANALYSIS	6-2
Dilution Sampler Filters.....	6-2
In-Stack Filters.....	6-4
ELEMENTAL (XRF) ANALYSIS	6-5
ORGANIC AND ELEMENTAL CARBON ANALYSIS	6-6
SULFATE, NITRATE, AND CHLORIDE, AND ANALYSIS.....	6-7
SVOC ANALYSIS	6-8
VOC ANALYSIS	6-9
CARBONYLS ANALYSIS.....	6-11
INORGANIC RESIDUE ANALYSIS	6-16
7.0 DISCUSSION AND FINDINGS.....	7-1
DILUTION SAMPLER MEASUREMENTS	7-1
Particulate OC.....	7-2
SULFATE COMPARISON.....	7-4
Dilution Sampler versus Method 202	7-4
Artifact Sulfate Formation in the Impingers.....	7-5
COMPARISON OF PURGED AND UNPURGED METHOD 202	
TRAIN DATA	7-6
COMPARISON TO PUBLISHED DATA.....	7-8
POTENTIAL EMISSIONS MARKER SPECIES.....	7-10
Organic Speciation Profile.....	7-12
FINDINGS.....	7-14
REFERENCES	R-1
Appendix A	
LIST OF ABBREVIATIONS.....	A-1
Appendix B	
SI CONVERSION FACTORS	B-1

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
ES-1 Speciation Profile for Primary Particulate Emissions from Gas-Fired Process Heater	ES-7
2-1 Heater Process Overview and Sampling/Monitoring Locations.....	2-2
3-1 Chronology for Gas-Fired Process Heater Tests (Site Alpha).....	3-3
3-2 PM10/PM2.5 Train Configuration for Method PRE-4/202	3-6
3-3 Modified Method 202 Sample Analysis Procedure	3-8
3-4 Dilution Sampling System	3-9
5-1 PM2.5 Speciation, as Measured by the Dilution Sampler (Site Alpha).....	5-9
5-2 Organic Aerosol Speciation (Site Alpha)	5-10
5-3 Method PRE-4/202 PM2.5 Mass Speciation Profile (Site Alpha).....	5-12
7-1 Site Alpha (Refinery Gas-Fired Process Heater) OC Results.....	7-4
7-2 Inorganic CPM Residue Speciation Results	7-7
7-3 Mass Speciation for Dilution Sampler Ambient and Stack Samples (Site Alpha)	7-11
7-4 Comparison of Average Sample Concentration and Detection Limits (Site Alpha) .	7-11
7-5 Average Sample Concentration Minus Ambient Concentration (Site Alpha).....	7-12

LIST OF TABLES

<u>Table</u>	<u>Page</u>
ES-1 Summary of Primary Particulate Emission Factors for a Gas-Fired Process Heater	ES-3
ES-2 Summary of Semivolatile Organic Species Emission Factors for a Gas-Fired Process Heater	ES-4
ES-3 Summary of Secondary Particulate Precursor Emission Factors for a Gas-Fired Process Heater	ES-6
1-1 Overview of Sampling Scope	1-4
1-2 Summary of Analytical Targets	1-5
3-1 Summary of Test Procedures	3-2
3-2 Dilution Sampler Operating Conditions	3-11
4-1 Approximate In-Stack Detection Limits Achieved for Gas-Fired Process Heater Tests (Site Alpha)	4-2
4-2 Process Operating Conditions (Site Alpha)	4-3
4-3 Fuel Gas Analysis (Site Alpha)	4-3
4-4 Fuel Gas Sulfur Speciation Results in ppmv (Site Alpha)	4-4
4-5 Average Stack Conditions (Site Alpha)	4-4
4-6 Filterable Particulate Matter Results (Site Alpha)	4-5
4-7 Condensible Particulate Matter (Method 202) Results (Site Alpha)	4-6
4-8 Speciation (mg/dscm) of Back-Half Impinger Catch (Site Alpha)	4-9
4-9 Dilution Sampler PM2.5 Results (Site Alpha)	4-10
4-10 Dilution Sampler Ion Results (Site Alpha)	4-11
4-11 OC/EC as Measured by the Dilution Sampler (Site Alpha)	4-12
4-12 Semi-Volatile Organic Compound (SVOC) Results (mg/dscm) (Site Alpha)	4-13
4-13 Volatile Organic Compound (VOC) Results from Tenax (Site Alpha)	4-15
4-14 Volatile Organic Compound (VOC) Results - Canisters (Site Alpha)	4-17
4-15 Elements, as Measured by the Dilution Sampler (Site Alpha)	4-20
4-16 Carbonyl Results (mg/dscm) (Site Alpha)	4-20
4-17 Secondary PM Precursor Results (Site Alpha)	4-21
5-1 Primary Emissions – Particulate Mass and Elements (Site Alpha)	5-2
5-2 Primary Emissions – Carbon and SVOCs (Site Alpha)	5-3
5-3 Secondary Fine PM Precursors (VOCs) -- Tenax (Site Alpha)	5-4
5-4 Secondary Fine PM Precursors (VOCs) – Canisters (Site Alpha)	5-5
5-5 Carbonyl (Aldehyde) Emission Factors (Site Alpha)	5-7
5-6 Secondary Particle Precursors (Site Alpha)	5-7
5-7 Speciation Profile for Primary Emissions – Dilution Sampler Results (Site Alpha)	5-8
5-8 Organic Aerosol Speciation Profile (Site Alpha)	5-10
5-9 Speciation Profile for PM2.5 Measured by Method PRE-4/202 (Site Alpha)	5-11
6-1 Pre- and Post-Test Flow Checks for the Dilution Sampler	6-3
6-2 Dilution Sampler PM2.5 blank Results (mg/dscm)	6-4
6-3 Filter and Reagent Blank Results	6-5
6-4 Results from Acetone Blank Rinses	6-5

LIST OF TABLES (CONTINUED)

<u>Table</u>	<u>Page</u>
6-5 XRF Elemental Analysis Field Blank Results (mg/dscm).....	6-6
6-6 Field Blank and Ambient Results – OC/EC Analysis	6-7
6-7 Ions and Secondary PM Precursor Blank Results (mg/dscm)	6-9
6-8 PUF/XAD Field Blank Results (mg/dscm).....	6-11
6-9 Tenax Field Blank (mg/dscm)	6-12
6-10 Canister Samples VOC's Blanks Results (Site Alpha).....	6-13
6-11 Carbonyls VOC's Blanks Results (Site Alpha)	6-16
6-12 Method 202 Water Reagent Blank Results (mg/dscm).....	6-16
7-1 PM Emission Factor Comparison	7-2
7-2 Organic Carbon and Backup Filter Organic Carbon Results (mg/dscm)	7-3
7-3 Comparison of Sulfate Measurements (mg/dscm).....	7-5
7-4 Results from Pilot Scale Evaluation of Purged versus Unpurged Method 202 Trains (mg/dscm)	7-8
7-5 Comparison of Data from Corio and Sherwell (2000) and Current Program.....	7-9
7-6 Comparison of EPA AP-42 Database and Current Program Data.....	7-9
7-7 Average Organic Aerosol Emission Factor Comparison (lb/MMBtu)	7-13

EXECUTIVE SUMMARY

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source receptor and source apportionment analysis;
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source receptor and source apportionment analysis; and
- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

This report presents emissions data from testing performed on a gas-fired process heater with no air pollution control devices. The flue gas temperature at the stack was approximately 795°F during the tests.

The PM measurements at the stack were made using both a dilution sampling test method and traditional hot filter/iced impinger methods used for regulatory enforcement of particulate regulations. The dilution sampling method is attractive because the sample collection media and analysis methods are identical to those used for ambient air sampling, thus the results are directly comparable with ambient air data. Also, the dilution sampling method is believed to provide representative results for solid, liquid and condensable aerosols together on a single analytical sample. While dilution sampling is widely accepted for demonstrating compliance with mobile source particulate emission standards and for stationary source receptor and source apportionment analysis, it is not currently accepted by regulatory agencies for demonstrating compliance with existing stationary source PM₁₀ emission standards or permit limits. The traditional regulatory methods are attractive because they are readily accepted by regulatory agencies and have been used extensively on a wide variety of source types; however, existing regulatory methods for condensable aerosols may be subject to significant bias and sampling/analytical options are limited.

The tests employed standard ambient air sample collection and analysis methods in conjunction with a developmental dilution sampling technique that extracted the stack gas sample and diluted it with ambient air prior to sample collection. The design of the dilution sampler follows the design established by Hildemann et al. (1989). In these and other tests of gas combustion sources, the dilution sampler results showed much lower PM_{2.5} concentration and markedly different PM_{2.5} chemical speciation compared to the traditional hot filter/iced impinger methods. Other studies suggest this is primarily due to artifacts and other limitations of the iced impinger methods when applied to gas combustion sources (Wien et al., 2001).

The average emission factors for all species measured were low, which is expected for gas-fired sources. Emission factors for primary particulate including: total particulate, PM₁₀ (particles smaller than nominally 10 micrometers), PM_{2.5} and condensable PM (CPM); elements; ionic

species; and organic and elemental carbon are presented in Table ES-1. Emission factors are expressed in pounds of pollutant per million British thermal units of gas fired (lb/MMBtu). Four six-hour runs were performed on separate, consecutive days. As a measure of the bias, precision, and variability of the results, the uncertainty (at the 95 percent confidence level) and upper 95 percent confidence bound also are presented. Emission factors with an uncertainty greater than 100 percent are not presented in the tables, as they are considered unrepresentative.

Emission factors for semivolatile organic compounds (SVOCs) are presented in Table ES-2. The sum of carbon from SVOCs is approximately five percent of the total organic carbon.

Table ES-1. Summary of Primary Particulate Emission Factors for a Gas-Fired Process Heater.

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
Particulate Mass	PM2.5 mass (Dilution Sampler)	< 5.23E-5	43	6.91E-5	3
Elements	S	1.39E-5	94	2.36E-5	4
	Si	9.98E-7	79	1.69E-6	4
Ions	NO ₃ ⁻	8.68E-6	77	1.37E-5	4
	SO ₄ ⁼	3.59E-5	92	6.06E-5	4
	Soluble Na	3.43E-7	43	4.70E-7	4
Particulate Mass (Manual methods)	Organic CPM (unpurged train)	1.06E-3 *	76	1.67E-3	4
	Inorganic CPM (unpurged train)	6.62E-3 *	98	1.14E-2	4
	Total CPM (unpurged train)	7.77E-3 *	93	1.32E-2	4
	Organic CPM (purged train)	1.61E-3 *	43	2.16E-3	4
	Inorganic CPM (purged train)	2.22E-2 *	57	3.18E-2	4
	Total CPM (purged train)	2.41E-2 *	53	3.39E-2	4
	Total Filterable PM (Method 17, unpurged train)	5.49E-4 *	36	7.06E-4	4
	Total Filterable PM (Method PRE-4, purged train)	8.89E-4 *	89	1.49E-3	4
	Filterable PM10 (Method PRE-4, purged train)	5.89E-4 *	75	9.23E-4	4
	Filterable PM2.5 (Method PRE-4, purged train)	4.36E-4 *	76	6.85E-4	4

* Emission factors not recommended for emission estimation purposes.

Table ES-2. Summary of Semivolatile Organic Species Emission Factors for a Gas-Fired Process Heater.

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
Organic Carbon	9.26E-5 *	21	1.11E-4	4
Total Carbon	1.03E-4	25	1.26E-4	4
Semi-Volatile Organic Compounds				
1+2-ethylnaphthalene	5.37E-7	72	8.31E-7	4
2,6+2,7-dimethylnaphthalene	8.57E-7	85	1.41E-6	4
1,3+1,6+1,7-dimethylnaphthalene	1.43E-6	84	2.33E-6	4
A-trimethylnaphthalene	2.70E-7	80	4.34E-7	4
1-ethyl-2-methylnaphthalene	1.00E-7	52	1.43E-7	4
B-trimethylnaphthalene	2.11E-7	68	3.21E-7	4
C-trimethylnaphthalene	2.31E-7	54	3.28E-7	4
2-ethyl-1-methylnaphthalene	< 1.02E-6	97	1.71E-6	3
E-trimethylnaphthalene	9.61E-8	66	1.47E-7	4
2,3,5+I-trimethylnaphthalene	1.47E-7	79	2.37E-7	4
J-trimethylnaphthalene	9.85E-8	56	1.42E-7	4
Phenanthrene	1.43E-7	91	2.43E-7	4
2-methylphenanthrene	2.96E-8	83	5.11E-8	4
Acenaphthylene	< 3.31E-7	76	5.24E-7	2
OC Backup Filter**	9.74E-5	37	1.30E-4	4

* OC is subject to potential positive bias from adsorption of VOC on the filter. Refer to Sections 6 & 7 for further discussion.

** OC measured on a backup" quartz fiber filter placed downstream of Teflon membrane filter - not included in sum of species calculations. Refer to Sections 6 & 7 for further discussion.

The preceding tables include only those substances that were detected in at least two of the four test runs. Substances of interest not present above the minimum detection limit for these tests are listed in Table ES-3.

The primary particulate emission factor results presented in Table ES-1 also may be expressed as a PM_{2.5} speciation profile (Figure ES-1), which is the mass fraction of each species contributing to the total PM_{2.5} mass as measured by the dilution sampler. The speciation profile should only be applied to PM_{2.5} mass obtained from dilution sampling; any application to emission factors obtained from manual methods will result in erroneous calculations; manual method results are presented for comparative purposes only.

The main findings of these tests are:

- Particulate mass emissions from the heater were extremely low, consistent with levels expected for gaseous fuel combustion. The low particulate loading

associated with gas combustion may contribute to the large uncertainties in the collected mass.

- Two methods for determining the average emission factor for primary PM_{2.5} mass gave results which differed by more than an order of magnitude: 5.2×10^{-5} lb/MMBtu using the dilution sampler; and 8.2×10^{-3} lb/MMBtu using conventional in-stack filters and iced impinger methods for filterable PM (FPM) and CPM, respectively.
- Sampling and analytical artifacts principally caused by gaseous SO₂ in the stack gas were shown to produce a relatively large positive bias in CPM as measured by conventional iced impinger train methods. These measurement artifacts can explain most of the difference between dilution sampling and conventional method results. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U.S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species were measured and when summed were approximately four times greater than the measured PM_{2.5} mass, assuming the highest stable oxide forms for metals.
 - Organic and elemental carbon together are almost two times higher than the primary PM_{2.5} mass measured on the Teflon[®]-membrane filter (TMF).
 - The quartz filter used for ion and carbon speciation is subject to organic absorptive bias, especially in low load sources, such as gas-fired heaters, so a likely source of this difference is the high organic carbon value. A backup quartz filter sampled behind the TMF indicated that almost all of the organic carbon might be due to adsorption bias.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods to provide representative emission factor data.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.

Table ES-3. Substances of Interest Not Detected in Stack Emissions from a Gas-Fired Process Heater.

Inorganic	VOC (>C2)	VOC (>C7)	SVOC
Antimony	3-methyl-1-pentene	4-ethyl-o-xylene	1,2-dimethylnaphthalene
Arsenic	4-methyl-1-pentene	4-n-propyltoluene + 1,4-diethylbenzene	1,4,5-trimethylnaphthalene
Barium	alpha-pinene	4-tert-butyltoluene	1,7-dimethylphenanthrene
Chromium	Chloroform	5-ethyl-m-xylene	1-MeFl+C-MeFl/Py
Cobalt	Isoprene	5-isopropyl-m-xylene	1-methylfluorene
Gallium	n-butylbenzene	Acenaphthene	1-methylphenanthrene
Gold	Undecene-1	Acenaphthylene	1-methylpyrene
Indium		A-dimethylindane	2,3-Benzofluorene
Lanthanum		alpha-Pinene	2,4,5-trimethylnaphthalene
Manganese		B-dimethylindane	2-Methylbiphenyl
Mercury		Benzoic acid	3,6-dimethylphenanthrene
Molybdenum		beta-pinene	3-Methylbiphenyl
Nickel	VOC (>C7)	Butyl acetate	4-Methylbiphenyl
Palladium	(+/-)-limonene	Butylbenzene	4-methylpyrene
Rubidium	1,2,3,4-tetrahydronaphthalene	Cyclohexanone	7-methylbenzo(a)pyrene
Selenium	1,2,3,4-tetramethylbenzene	D-dimethylindan	9-Anthraldehyde
Silver	1,2,3,5-tetramethylbenzene	Dimethyloctane	9-methylanthracene
Strontium	1,2,3-trimethylbenzene	Eicosane	Acenaphthene
Thallium	1,2,4,5-tetramethylbenzene	Fluorene	Acenaphthenequinone
Tin	1,2-dichlorobenzene	Heptadecane	A-dimethylphenanthrene
Uranium	1,2-diethylbenzene	Hexadecane	A-MePy/MeFl
Yttrium	1,2-dihydronaphthalene	Hexyl acetate	A-methylfluorene
Zirconium	1,2-dimethylnaphthalene	Indan	A-methylphenanthrene
Carbonyl	1,3-diethylbenzene	Isoamylbenzene	Anthraquinone
Acrolein	1,3-diisopropylbenzene	Isobutylbenzene	B-dimethylphenanthrene
Propionaldehyde	1,4-diisopropylbenzene	Isopropylbenzene	Benz(a)anthracene-7,12-dionene
Crotonaldehyde	1,6+1,3+1,7-dimethylnaphthalene	m-isopropyltoluene	Benzo(b+j+k)fluoranthene
MEK	1+2-ethylnaphthalene	m-tolualdehyde	Benzo(c)phenanthrene
Methacrolein	1-decene	Nonadecane	Benzonaphthothiophene
Butyraldehyde	1-methylindan	Octadecane	Bibenzyl
Benzaldehyde	1-methylnaphthalene	Octanal	B-methylfluorene
Valeraldehyde	2-(2-butoxyethoxy) ethanol	o-isopropyltoluene	B-methylphenanthrene
M-Tolualdehyde	2,3+1,5+1,4-dimethylnaphthalene	o-methylphenol	C-methylphenanthrene
Hexanaldehyde	2,6+2,7-dimethylnaphthalene	Pentamethylbenzene	Coronene
VOC (>C2)	2-butoxyethyl acetate	Pentylbenzene	Dibenzo(ah+ac)anthracene
1 & 2-butyne	2-decanone	Phenanthrene	Dibenzofuran
1,3-dimethyl-4-ethylbenzene	2-ethyl-p-xylene	p-isopropyltoluene	Fluorene
2,2,3-trimethylbutane	2-methylbenzofuran	Propylcyclohexane	F-trimethylnaphthalene
2,2-dimethylpentane	2-methylindan	Propylene glycol	Indeno[123-cd]pyrene
2,4-dimethylheptane	2-methyloctane	Sec-butylbenzene	Perinaphthenone
2-methylindan	2-n-propyltoluene	t-2-heptenal	Perylene
2-methyloctane	2-pentylfuran	t-butylbenzene	Retene
2-methylpropanal	3-methyloctane	Tridecane	Xanthone

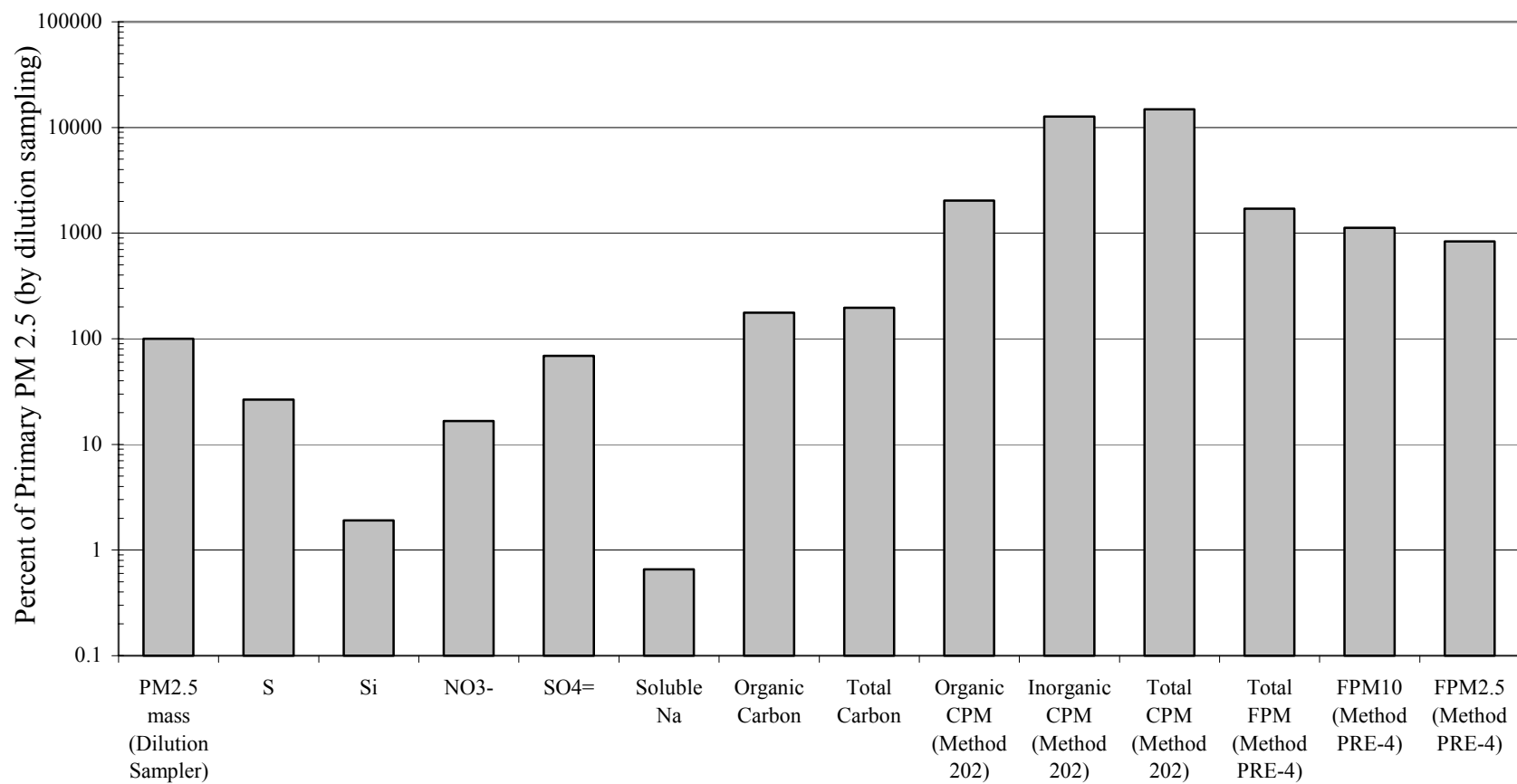


Figure ES-1. Speciation Profile for Primary PM Emissions from a Gas-Fired Process Heater.

Section 1

PROJECT DESCRIPTION

PROJECT OVERVIEW

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM_{2.5} measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1997), which concluded that dilution sampling techniques are more appropriate for obtaining a representative sample from combustion systems. These techniques have been widely used in research studies (e.g., Hildemann et al., 1994; McDonald et al., 1998), using clean ambient air to dilute the stack gas sample and providing 80-90 seconds residence time for aerosol formation prior to sample collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

Dilution sampling was used to collect PM emissions data from a gas-fired process heater at Site Alpha on February 15, 16, 20 and 21 2001, along with emissions data obtained from conventional sampling methods. The U.S. Department of Energy (DOE), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and API jointly funded the tests. This test program is designed to provide reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations.

The goals of this program were to:

- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source receptor and source apportionment analysis;
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source receptor and source apportionment analysis; and
- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.

It should be noted that the project team chose to complete the process heater test in advance of a pilot scale study of the dilution sampler test method to address a compelling need for detailed data on fine and ultrafine particulate emissions. The pilot-scale study is evaluating dilution ratio and residence time design criteria established by Hildemann et al. (1989) as part of the development of a more compact and field portable sampler that gives comparable results. A dilution sampler based on the original Hildemann design was used for this test.

PROJECT OBJECTIVES

The specific objectives of this test were to:

Primary Objectives

- Compare PM_{2.5} mass measured using an in-stack filter and iced impinger train (EPA Method PRE-4/202) and mass measured using a dilution sampler;
- Develop emission factors and speciation profiles for organic aerosols and PM_{2.5} mass;

- Characterize sulfate, nitrate, ammonium, inorganic elements, elemental carbon (EC) and organic carbon (OC) in PM collected on filter media in the dilution sampler;
- Characterize key secondary particle precursors in stack gas samples: volatile organic compounds (VOC) with carbon number of 7 and above carbonyls, benzene, toluene and xylenes; sulfur dioxide (SO₂); and oxides of nitrogen (NO_x); and
- Determine the effect of a post-test nitrogen purge on CPM results.
- Characterize semi volatile organic compounds (SVOC) speciation (for PM_{2.5} source apportionment);
- Compare emission factors obtained from test with similar emission factors currently available; and
- Identify issues associated with PM measurement from sources with relatively dilute exhaust streams.

TEST OVERVIEW

The scope of testing is summarized in Table 1-1. The emissions testing included simultaneous collection and analysis of both in-stack and diluted stack gas samples. All emission samples were collected from the exhaust stack of the unit downstream of all combustion processes and emission controls. The samples were analyzed for the compounds listed in Table 1-2. Process data and fuel gas samples were collected during the tests to document operating conditions.

CPM, ammonia and formaldehyde were measured by collection in iced impinger trains.

Source Level (Undiluted Exhaust Gas) Samples

In-stack sampling and analysis for filterable PM (total PM, PM with aerodynamic diameter less than 10 micrometers (PM₁₀) and PM_{2.5}) and CPM was performed using traditional EPA methods. In-stack cyclones and filters were used for FPM. CPM was measured by collection in iced impinger trains.

Table 1-1. Overview of Sampling Scope.

Sampling Location	Number of Samples		
	Fuel Gas Header	Stack	Ambient Air
EPA Method PRE-4/202 train	--	4	--
EPA Method 17/202 Train	--	4	--
Dilution sampler Teflon [®] filter Quartz filter K ₂ CO ₃ -impregnated cellulose fiber filter Citric acid-impregnated cellulose fiber filter TIGF/PUF/XAD-4 Tenax Stainless steel canisters DNPH-coated silica gel cartridges	--	4	1
Fuel sample	4	--	--
NO _x , CO, O ₂	--	Continuous	--
Process monitoring	--	Continuous	--

TIGF - Teflon[®]-impregnated glass fiber filter

PUF - polyurethane foam

XAD-4 - Amberlite[®] sorbent resin

DNPH - dinitrophenylhydrazine

Diluted Exhaust Gas Samples

Dilution sampling was used to characterize PM_{2.5} including aerosols formed in the near-field plume. The dilution sampler extracted a sample stream from the stack into a mixing chamber, where it was diluted approximately 21:1 with ambient air purified by passing through a HEPA filter and activated carbon. Because PM_{2.5} behaves aerodynamically almost like a gas at typical stack conditions, the samples were extracted nonisokinetically. A slipstream of the mixed and diluted sample was conveyed to a residence time chamber where it resided for approximately 70 seconds to allow time for low-concentration aerosols, especially organics, to condense and grow. The diluted and aged sample then passed through cyclone separators sized to remove particles larger than 2.5 microns, after which samples were collected on various media: high-purity quartz

Table 1-2. Summary of Analytical Targets.

Parameters	In-Stack				Dilution Sampler								
	Cyclones	Quartz filter	Imp.	Gases	Quartz filter	TIGF /PUF/ XAD	TMF	Tenax	SS cans	DNPH cartridges	K ₂ CO ₃ filter	Citric acid filter	Gases
Total PM mass	X	X											
PM10 mass	X	X											
PM2.5 mass	X	X					X						
CPM mass			X										
Sulfate			X		X								
Chloride			X		X								
Ammonium			X		X								
Nitrate			X		X								
Elements			X				X						
Organic carbon					X								
Elemental carbon					X								
Semivolatile organic compounds						X							
Volatile organic compounds*								X					
Volatile organic compounds**									X				
Carbonyls										X			
Ammonia (gaseous)												X	
NO _x				X									
SO ₂											X		
CO				X									
O ₂				X									
Moisture or relative humidity			X										X
Velocity				X									
Temperature				X									X

TMF - Teflon® membrane filter

TIGF - Teflon®-impregnated glass fiber filter

DNPH – dinitrophenylhydrazine

SS cans – stainless steel canisters

Imp. – iced impinger train

*Carbon number of 7 or greater

**Carbon number of 2 to 10

for ions and carbon speciation, Teflon® membrane filter (TMF) for PM2.5 mass and elements, potassium carbonate-impregnated cellulose fiber for SO₂, citric acid-impregnated cellulose fiber for ammonia and Teflon®-impregnated glass fiber (TIGF) filters for particle phase SVOCs; a polyurethane foam (PUF)/Amberlite® sorbent resin (XAD-4)/PUF cartridge to collect gas phase SVOCs; Tenax tubes to capture VOCs with a carbon number greater than seven; a stainless steel canister to capture VOCs with a carbon number greater than two; and dinitrophenylhydrazine

(DNPH)-coated silica gel cartridges to capture carbonyls (aldehydes). Four samples were collected over six hours on four separate test days.

An ambient air sample was collected to establish background concentrations of measured substances. The same sampling and analysis procedures used for the dilution sampler were applied for collecting ambient air samples.

Process Samples

A sample of the fuel gas burned in the process heater was collected on each day of source testing and analyzed for specific gravity, heating value, sulfur species and hydrocarbon species.

KEY PERSONNEL

GE Energy and Environmental Research Corporation (GE EER) had overall responsibility for the test program. Key personnel and managers involved in the tests were:

- Glenn England (GE EER) – Program Manager (949) 859-8851 ext. 136
- Stephanie Wien (GE EER) – Project Engineer (949) 859-8851 ext. 155
- Bob Zimperman (GE EER) – Field Team Leader (949) 552-1803
- Judith Chow, John Watson, and Barbara Zielinska (Desert Research Institute (DRI)) – Consulting and Laboratory Analysis (775) 674-7050
- Karl Loos (Shell Global Solutions U.S.) – API Work Group Chairman (281) 544-7268
- Karin Ritter (API) – API Project Officer (202) 682-8472
- Jim McCarthy and Paul Drayton (GRI) – GRI Project Manager (847) 768-0694)
- Guido Franco and Marla Mueller (CEC) – CEC Project Manager (916) 654-4894)
- Dan Gurney and Kathy Stirling (DOE) – DOE Contracting Officer Representative (918) 699-2008)
- Barry Liebowitz (NYSERDA) – NYSERDA Project Manager (518) 862-1090 ext. 3248

Section 2

PROCESS DESCRIPTION

The tests were performed on a refinery gas-fired process heater at Site Alpha. The stack serves two heaters: Heater A has a maximum total heat input of 78.9 MMBtu/hr and Heater B has a maximum heat input of 106 MMBtu/hr. Heater A is the fluid catalytic cracking unit (FCCU) feed heater with 48 direct firing pre-mix burners in the firebox. Heater B provides hot oil to heat the unit recovery distillation columns, and utilizes up to 68 burners. Both heaters vent flue gas by way of natural draft. The unit has no NO_x emission control equipment. Operating conditions during the test are given in Section 4. Process parameters monitored during testing include: burner gas rate, inlet water rate, steam quality, radiant section, steam and stack temperature, and excess oxygen.

SAMPLING LOCATIONS

Figure 2-1 provides an overview of the heater process and the sampling and monitoring locations. Flue gas samples were collected from the stack. The single stack is equipped with a 360 degree circular sampling platform that is 47 inches wide and located approximately 90 feet above the ground. The stack is brick and cement lined. There are four four-inch diameter flanged sampling ports on the stack, which are at 90 degrees to one another. The stack diameter at this elevation is 132.5 inches. The sample ports are located 43 feet (3.9 diameters) downstream and 31 feet (2.8 diameters) upstream of the nearest flow disturbance. The flue gas concentration profile shows no stratification and there is no cyclonic flow present, based on previous testing at the unit. Preliminary velocity traverses were performed to determine average velocity in the stack. Due to the small port size, probes could not be co-located through single ports. Sampling was performed through three separate ports at points of average flow, as determined by the velocity traverses.

Fuel gas samples were collected from the gas supply fuel-sampling manifold. Ambient air samples were collected at ground-level close to the air inlet for the process heater.

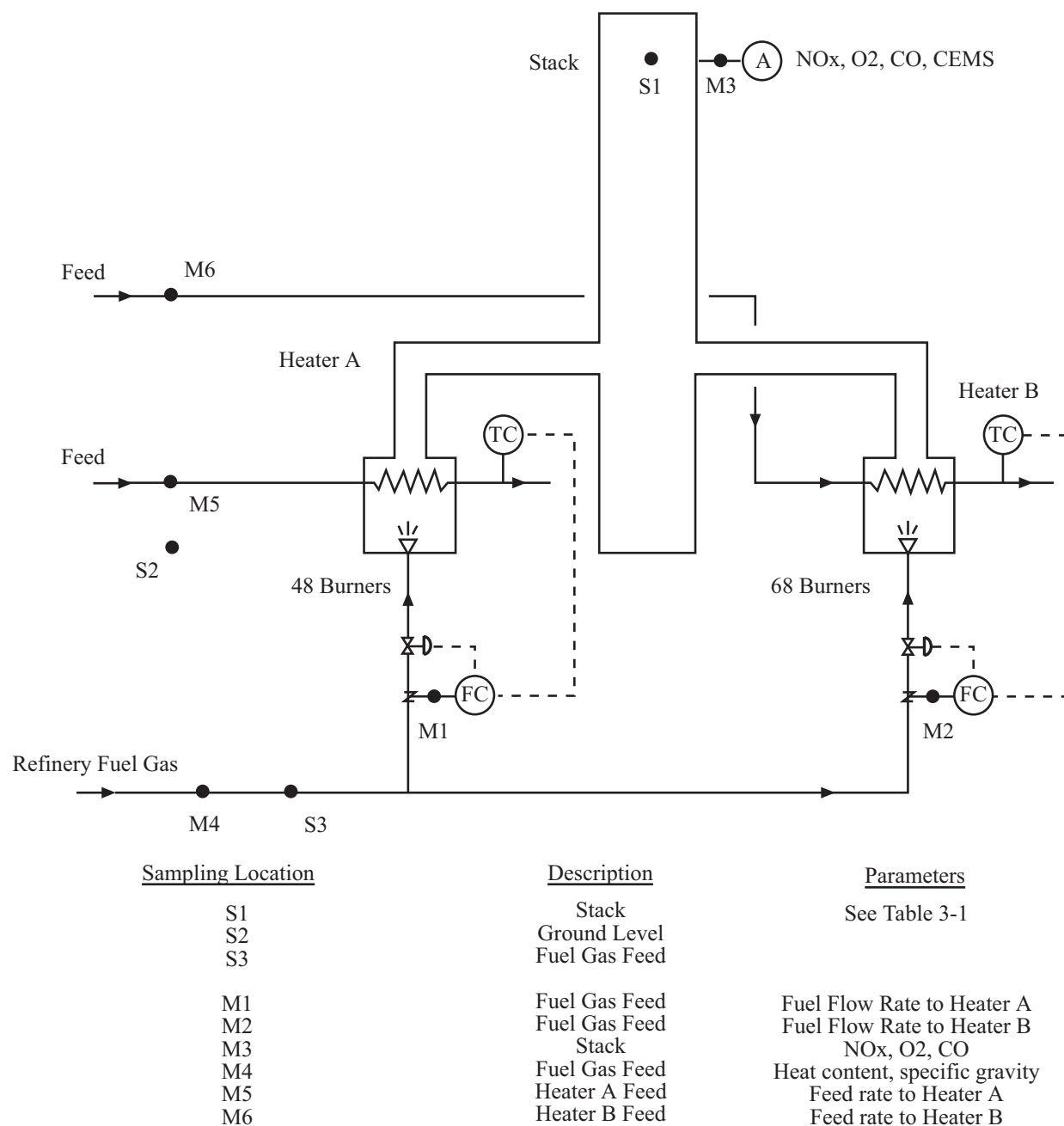


Figure 2-1. Heater Process Overview and Sampling/Monitoring Locations.

Section 3

TEST PROCEDURES

An overview of the sampling and analysis procedures is given in Table 3-1. Figure 3-1 shows the testing chronology for the dilution sampling and in-stack methods. The time of day for the start and finish of each measurement run is shown on the figure. For example, Method PRE-4/202 Run 1 began at 12:55 hours and finished at 17:57 hours on Thursday, February 15.

Dilution sampling and in-stack testing were performed concurrently. All samples were collected at points of average flow through their respective ports to allow for comparability of results, since it is assumed that the fine PM will follow the gas streamlines and hence be as well-mixed as the gases. Testing during Run 1 was halted before the 6-hour sample time due to a process upset that caused the unit to shut down. A sample run time of six hours was chosen so that sufficient material would be collected to exceed detection limits.

STACK GAS FLOW RATE, MOISTURE CONTENT AND MOLECULAR WEIGHT

An S-type Pitot tube (EPA Method 2) was used to determine the average stack gas velocity and volumetric flow rate. Stack gas molecular weight was calculated in accordance with EPA Method 3. Moisture content of the sample was determined based on weight gain of the impingers used in the Method 201A/202 train according to EPA Method 4. A full velocity traverse of the stack was performed before and after each test to determine total stack gas flow rate.

O₂, CO₂, CO, AND NO_x

Major gases and pollutant concentrations in the stack sample were monitored using the plant's continuous emission monitoring system (CEMS), which is operated and maintained in accordance with EPA 40 CFR 60 Appendix B.

IN-STACK METHOD TESTS

Total PM, PM₁₀ and PM_{2.5} filterable at stack temperature were determined using in-stack methods. CPM, defined as the material collected in chilled impingers, also was measured for the in-stack samples.

Table 3-1. Summary of Test Procedures.

Sampling Location	Measurements	Sampling Approach	Sample Analyses	Reference
S1 (Stack)	Total PM, PM10, PM2.5 and composition	In-stack series cyclones and filter	Mass; organic species	U.S. EPA Method PRE-4 (preliminary method)
	Condensable PM and composition	Impingers	Mass (organic and inorganic), sulfate, chloride, nitrate, ammonium, elements	U.S. EPA Method 202
S1 (Stack)	PM2.5 mass and chemical composition	Dilution sampler and filters	Mass, organic carbon (OC), elemental carbon (EC), elements, sulfate, nitrate, chloride, ammonium	U.S. EPA, 1999a; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution sampler and K ₂ CO ₃ -impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution sampler and citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Dilution sampler and Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Dilution sampler and stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Gaseous PM2.5 precursors	Dilution sampler and DNPH-coated silica gel cartridges	Carbonyls	UP EPA Method TO-11A
	SVOC	Dilution sampler and filter/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S2 (Ground level – ambient air)	PM2.5 and chemical composition	Filters	Mass, OC, EC, elements, chloride, sulfate, nitrate, ammonium	U.S. EPA, 1999a
	Gaseous PM2.5 precursors	Potassium carbonate-impregnated cellulose-fiber filter	Ammonia	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Citric acid-impregnated cellulose-fiber filter	Sulfur dioxide	Chow and Watson, 1998
	Gaseous PM2.5 precursors	Tenax	Speciated VOC (C7 and greater)	Zielinska et al., 1996; Hildemann et al., 1989
	Gaseous PM2.5 precursors	Stainless steel canisters	Speciated VOC (C2 and greater)	US EPA Method TO-15
	Gaseous PM2.5 precursors	DNPH-coated silica gel cartridges	Carbonyls	UP EPA Method TO-11A
	SVOC	TIGF/PUF/XAD-4/PUF	Speciated SVOC	U.S. EPA Method TO-13; Hildemann et al., 1989
S3 (Fuel gas feed to heater)	Fuel gas composition	Integrated grab sample (Tedlar bag)	Hydrocarbon speciation, CHON, sulfur content and heating value	ASTM D3588-91

	Time	Heater Stack				Process Samples
		Velocity	Method PRE-4/202	Method 17/202	Dilution Sampler	Fuel Sample
14-Feb-01 Wed.	9:00					
	10:00					
	11:00					
	12:00					
	13:00					
	14:00					
	15:00	Preliminary				
15-Feb-01 Thurs.	16:00					
	8:00					
	9:00	9:15-9:30				
	10:00					
	11:00		Run 1	Run 1	Run 1	
	12:00		12:55	12:55	12:55	
	13:00					
	14:00					14:37
	15:00					
	16:00					
16-Feb-01 Fri.	17:00		17:57	17:57	17:57	
	18:00					
	8:00		Run 1 purge			
	9:00					
	10:00					
	11:00					
	12:00					
	13:00					
	14:00					
	15:00	15:00-15:15	Run 2	Run 3	Run 4	
	16:00		16:00	16:00	16:00	16:50
	17:00					
	18:00					
	19:00					
	20:00					
	21:00		22:00	22:00	22:00	
	22:00					
	23:00	23:05-23:20				

Figure 3-1. Chronology for Refinery Gas-Fired Process Heater Tests (Site Alpha).

	Time	Heater Stack				Process Samples
		Velocity	Method PRE-4/202	Method 17/202	Dilution Sampler	Fuel Sample
20-Feb-01 Tues.	8:00	8:51	Run 2 purge			
	9:00	9:12	08:45-09:45			
	10:00					
	11:00		Run 3	Run 3	Run 3	
	12:00		12:00	12:00	12:00	
	13:00					13:10
	14:00					
	15:00					
	16:00					
	17:00		18:00	18:00	18:00	
	18:00		Purge			
	19:00	19:33-19:55	18:50-19:50			
21-Feb-01 Wed.	8:00	8:57				
	9:00	9:20				
	10:00		Run 4	Run 4	Run 4	
	11:00		11:00	11:00	11:00	
	12:00					12:30
	13:00					
	14:00					
	15:00					
	16:00		17:00	17:00	17:00	
	17:00		Purge			
	18:00	18:00	17:50-18:50			
	19:00	19:04				
22-Feb-01 Thurs.	8:00					
	9:00					
	10:00					
	11:00				11:20	
	12:00					
	13:00					
	14:00					
	15:00					
	16:00					
	17:00				17:20	
	18:00					
	19:00					

Figure 3-1. Chronology for Refinery Gas-Fired Process Heater Tests (Site Alpha) (continued).

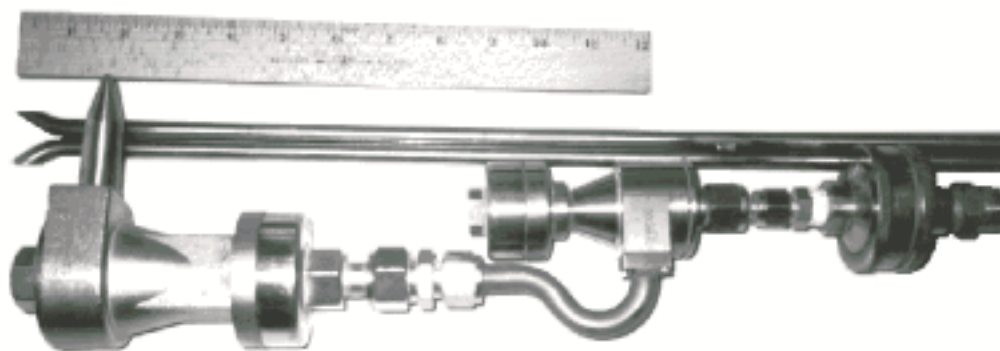
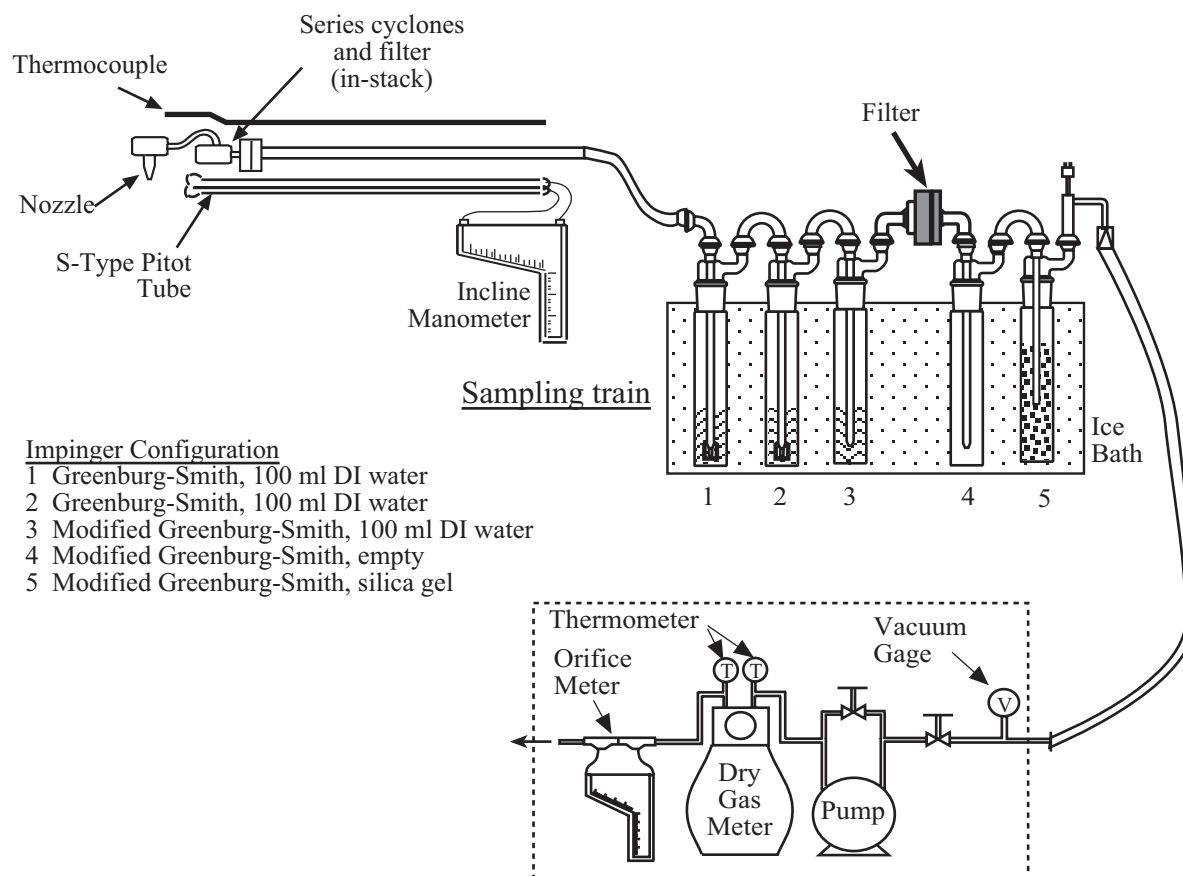
In-Stack Total Filterable PM, PM10 and PM2.5

EPA Preliminary Method PRE-4 was used to measure total PM, PM10 and PM2.5. The method uses two in-stack cyclones (Andersen Model Case-PM10 and Case-PM2.5), the first with a cut point of 10 microns and the second with a cut point of 2.5 microns, followed by an in-stack filter in series (Figure 3-2). The sampling time was six hours at a sampling rate of approximately 0.4 cubic feet per minute (cfm) for each of the four runs. Sampling was performed according to the methods as published except for the following modifications and clarifications:

- The sample was collected from a single traverse point near a point of average velocity to preserve the integrity of the dilution sampling method comparison. It is assumed that any PM present is small enough to mix aerodynamically in the same manner as a gas; therefore, the magnitude of the particle concentration profile was assumed to be no greater than the gas concentration profile;
- A modified filter assembly was employed in an effort to improve the precision of the gravimetric analysis for low PM concentration. An o-ring, a filter and a filter support are all placed together in an aluminum foil pouch and weighed as a unit. All three components are recovered together into the same foil pouch after sampling to minimize negative bias due to filter breakage.

A second PM train was run in order to compare the effect of post-test purging on the CPM catch. The front half of the second train was performed in accordance with EPA Method 17, which uses an in-stack filter to determine total PM emissions. The back half of this train was identical to the back-half of the EPA Method PRE-4 train.

The PM mass collected in the two cyclones and on the filter was determined gravimetrically. The filters (Pallflex Tissuequartz 2500QAT-UP-47mm) were weighed before and after testing on an analytical balance with a sensitivity of 10 micrograms. In an effort to improve the accuracy and precision of the gravimetric results, the filters, filter support and stainless steel O-ring seals were weighed together to minimize post-test loss of filter matter during sample recovery. Pre- and post-test weighing was performed after drying the filters in a dessicator for a minimum of 72 hours, and then repeat weighings were performed at a minimum of six-hour intervals until constant weight to within 0.5 milligrams was achieved. Probe and cyclone acetone rinses were recovered in glass sample jars for storage and shipment, and then transferred to tared beakers for



Series cyclone and filter assembly

Figure 3-2. PM10/PM2.5 Train Configuration for Method PRE-4/202.

evaporation and weighing. Acetone and filter blanks also were collected and analyzed. See Section 4 for discussion of data treatment.

Condensable Particulate Matter Mass and Chemical Analysis

CPM was determined using EPA Method 202; total sampling time was six hours for all runs. After the in-stack filter for the Method PRE-4 train, the sample passed through a heated Teflon[®] line to a series of four impingers placed in the ice bath. Impingers 1 and 2 were standard Greenburg-Smith impingers containing distilled deionized (DI) water; the third was a modified Greenburg-Smith impinger containing DI water; the fourth was an empty modified Greenburg-Smith impinger; and the fifth contained silica gel. A quartz filter (Pallflex Tissuequartz 2500QAT-UP) was placed between the third and fourth impingers to improve capture efficiency for any aerosols that may have passed the first three impingers. In order to examine the effect of a post-test nitrogen purge on CPM collected by Method 202, the impinger train of the EPA Method PRE-4 assembly was purged with nitrogen for one hour at the conclusion of each test run to eliminate dissolved SO₂. The impinger train of the EPA Method 17 assembly was not purged. The contents of both impinger trains were recovered separately with DI water followed by dichloromethane.

Previous tests (England et al., 2000) found that a majority (greater than 85 percent) of the PM emissions from gas-fired sources consists of CPM. To obtain an understanding of the composition of the material collected in the impingers, additional analysis of the inorganic CPM residue was performed to speciate its constituents. The inorganic residue was resuspended in DI water and analyzed for anions and cations (bromide, chloride, fluoride, nitrate, phosphate and sulfate) by ion chromatography, for ammonium by colorimetry, and for metals by digesting the sample in acid and analyzing by inductively coupled plasma – mass spectrometry (ICP/MS). Figure 3-3 illustrates the Method 202 analytical procedure and additional analyses performed.

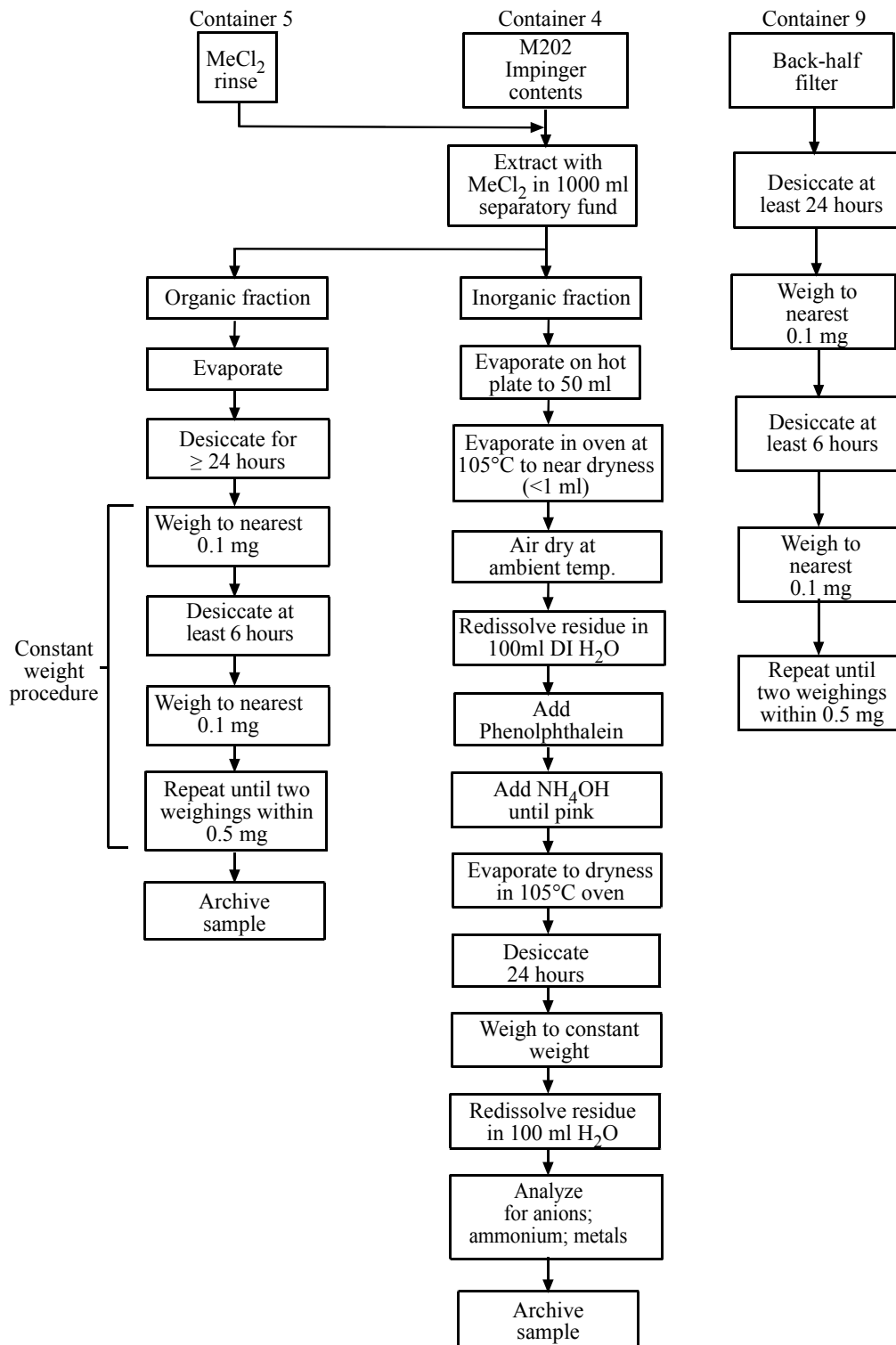


Figure 3-3. Modified Method 202 Sample Analysis Procedure.

DILUTION SAMPLER TESTS

PM_{2.5} mass and chemical speciation in the stack gas was determined using a dilution sampler (Figure 3-4). A stainless steel probe with a buttonhook nozzle was used to withdraw gas from the stack; the sample was transported from the probe through a heated copper line into the dilution sampler.

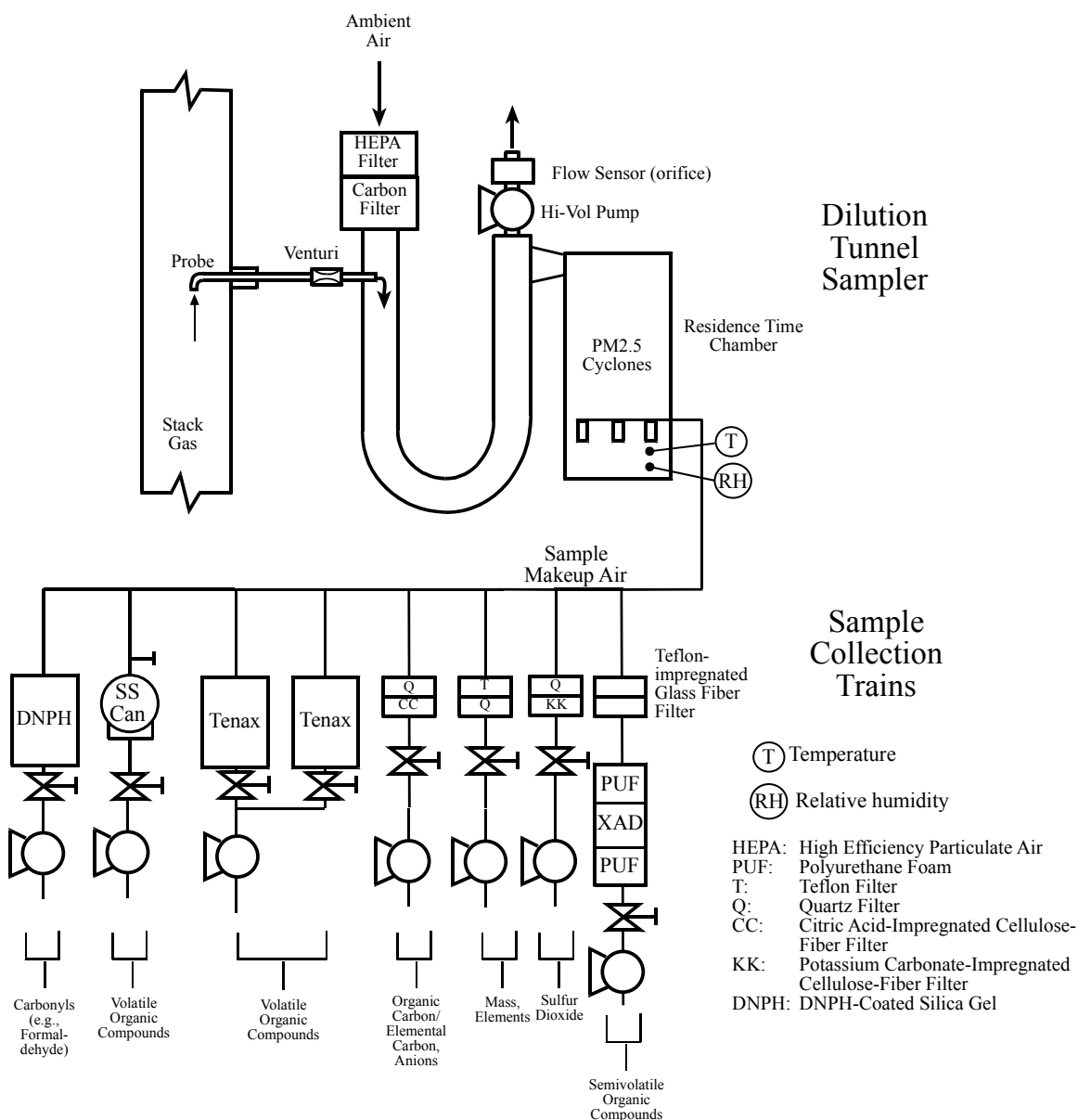


Figure 3-4. Dilution Sampling System.

The stack gas was mixed in the sampler with purified ambient air under turbulent flow conditions to cool and dilute the sample to near-ambient conditions. The ambient air used for dilution was purified using a high efficiency particulate air (HEPA) filter to remove PM and an activated carbon bed to remove gaseous organic compounds. After passing through a tube length equal to 10 tube diameters, approximately 50 percent of the diluted sample was withdrawn into a large chamber, where the sample aged for approximately 70 seconds to allow low-concentration aerosols (especially organic aerosols) to fully form. The aged sample was withdrawn through a sampling manifold of three cyclone separators to remove particles larger than 2.5 μm into a sampling module to provide a uniform gas stream for the sample collection media (TMF, quartz filter, K_2CO_3 -impregnated cellulose-fiber filter, citric acid-impregnated cellulose-fiber filter, Tenax tubes, DNPH-coated silica gel cartridges, stainless steel canisters and TIGF/PUF/XAD-4/PUF cartridge). The sample flow rate through the probe was monitored using a venturi flow meter and thermocouple. The venturi velocity head was measured continuously during the test using a pressure transducer and a Magnehelic[®] gauge. An S-type Pitot tube with electronic pressure transducer and thermocouple were used to monitor the velocity in the stack. The thermocouples and pressure transducers were connected to a laptop computer data acquisition system. The dilution airflow and backpressure were adjusted to maintain the target dilution ratio and sample flow rates. Total sampling time for each test run was six hours.

For these tests, flow rates were set in the field to achieve a target dilution ratio of approximately 30:1 (dilution air:sample) to improve minimum detection limits since very low concentrations of the target substances were anticipated. The prior work of Hildemann et al. (1989) suggests that mixing between the sample and the dilution air begins to degrade below a dilution ratio of approximately 20:1. This program is evaluating and optimizing design parameters, including dilution ratio, in a separate pilot scale evaluation of the dilution sampling method, with results to be presented in a separate report.

A single ambient air sample was collected using the dilution sampler. The sampling setup was modified by attaching a three-cyclone manifold (similar to the one inside the residence time chamber) directly to the sampling module without the use of the dilution sampler. The ambient air sample was drawn into the module without dilution or filtration for a sampling period of six

hours. The same sampling media were used as described below and in Figure 3-4. The ambient air sample was collected at ground level, close to the combustion air inlet for the heater.

Dilution sampler operating conditions during the test are listed in Table 3-2.

Table 3-2. Dilution Sampler Operating Conditions.

Parameter	Units	Run 1 15-Feb-01	Run 2 16-Feb-01	Run 3 20-Feb-01	Run 4 21-Feb-01	Ambient 22-Feb-01
Ambient Air Temp.	°C	15.6	16.9	18.3	19.1	15.5
Ambient RH	%	61.3	79.2	72.2	63.6	70.5
Dilution Chamber Temp.	°C	18.4	18.6	20.7	21.7	NA
Dilution Chamber RH	%	68.5	87.2	85.3	73.0	NA
Stack Sample Flow Rate	dry slpm	16.7	17.2	17.1	17.1	NA
Dilution Ratio	--	35.0	35.4	35.5	34.9	NA
Teflon Filter Flow Rate (mass, elements)	dry slpm	73.7	75.7	74.8	74.4	74.6
Quartz Filter Flow Rate (ions, OC/EC)	dry slpm	76.0	75.7	76.0	75.6	75.8
Citric Acid Filter Flow Rate (NH ₃)	dry slpm	76.0	75.7	76.0	75.6	75.8
K ₂ CO ₃ Filter Flow Rate (SO ₂)	dry slpm	76.0	74.5	78.4	76.7	76.9

NA – not applicable

RH – relative humidity

slpm – standard liters per minute

PM2.5 Mass

Samples for PM2.5 mass measurements were collected on a 47-mm diameter polymethylpentane ringed, 2.0 micron (µm) pore size, TMF (Gelman No. RPJ047) placed in a two-stage Savillex filter holder. The filter packs were plugged directly into the bottom of the sampling module to ensure that no handling of the filters was required in the field. The flow rate through the filter was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the inlet side of the filter pack and setting the position of the needle valve to achieve the desired flow rate of 160 standard cubic feet per hour (scfh). Weighing was performed on a Cahn 31 electro-microbalance with a one-microgram sensitivity.

Elements

Energy dispersive x-ray fluorescence (ED-XRF) analysis was performed on the TMFs for the following 40 elements: aluminum (Al), silver (Ag), arsenic (As), gold (Au), barium (Ba), bromine (Br), calcium (Ca), cadmium (Cd), chlorine (Cl), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), indium (In), potassium (K), lanthanum (La), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus

(P), lead (Pb), palladium (Pd), rubidium (Rb), sulfur (S), antimony (Sb), selenium (Se), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), thallium (Tl), uranium (U), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr). Mg and Na results are considered semiquantitative because of analytical technique limitations.

A Kevex Corporation Model 700/8000 ED-XRF analyzer with a side-window, liquid-cooled, 60 kilo electron volts (keV), 3.3 milliamp rhodium anode x-ray tube and secondary fluorescers was used. The silicon detector had an active area of 30 square millimeters, with a system resolution better than 165 electron volts (eV). The analysis was controlled, spectra were acquired, and elemental concentrations were calculated by software on a microcomputer, which was interfaced to the analyzer. Five separate x-ray fluorescence (XRF) analyses were conducted on each sample to optimize the detection limits for the specified elements. The filters were removed from their petri slides and placed with their deposit sides downward into polycarbonate filter cassettes. A polycarbonate retainer ring kept the filter flat against the bottom of the cassette. The cassettes were loaded into a carousel in the x-ray chamber. The sample chamber was evacuated to 10^{-3} Torr. A computer program controlled the positioning of the samples and the excitation conditions. Complete analysis of 16 samples under five excitation conditions required approximately 6 hours.

Sulfate, Nitrate, Chloride and Ammonium

Samples for determining water-soluble Cl^- , nitrate (NO_3^-), and $\text{SO}_4^{=}$ were collected on 47 mm quartz fiber filters (Pallflex Tissuequartz 2500QAT-UP-47mm). The flow rate through the filter was set prior to sample collection and checked after sample collection by placing a calibrated rotameter on the inlet side of the filter pack and setting the position of the needle valve to achieve the desired flow rate of 160 scfh.

Each quartz-fiber filter was cut in half, and one filter half was placed in a polystyrene extraction vial with 15 ml of DI water. The remaining half was used for determination of OC and EC as described below. The extraction vials were capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material. After extraction, these solutions were stored under refrigeration prior to analysis. Cl^- , NO_3^- , and $\text{SO}_4^{=}$

were measured with a Dionex 2020i ion chromatograph (IC). Approximately 2 ml of the filter extract was injected into the ion chromatograph.

A Technicon TRAACS 800 Automated Colorimetric System (AC) was used to measure NH_4^+ concentrations by the indolphenol method. Each sample was mixed with reagents and subjected to appropriate reaction periods before submission to the colorimeter. Beer's Law relates the liquid's absorbency to the amount of the ion in the sample. A photomultiplier tube measured this absorbency through an interference filter specific to NH_4^+ . Two milliliters of extract in a sample vial were placed in a computer-controlled autosampler. Technicon software operating on a microcomputer controlled the sample throughput, calculated concentrations, and recorded data.

Organic and Elemental Carbon

Quartz fiber filters (Pallflex Tissuequartz 2500QAT-UP-47mm) were used to collect samples for determination of OC and EC mass (see above). The filters were heated in air for at least three hours at approximately 900°C prior to use. Pre-acceptance testing was performed on each lot of filters. Filters with levels exceeding 1.5 micrograms per square centimeter ($\mu\text{g}/\text{cm}^2$) of OC and 0.5 $\mu\text{g}/\text{cm}^2$ of EC were refired or rejected. Pre-fired filters were sealed and stored in a freezer prior to preparation for field sampling.

The thermal/optical reflectance (TOR) method (IMPROVE protocol) was used to determine OC and EC on the quartz filters. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The TOR carbon analyzer consists of a thermal system and an optical system. Reflected light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion of carbon that takes place during OC analysis. After oxygen is introduced, the reflectance increases rapidly as the light-absorbing carbon burns off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is defined as EC.

Volatile Organic Compounds

Tenax. Glass tubes filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent were used to collect VOC samples. Two Tenax cartridges in parallel were used simultaneously for each test run due to the low concentrations expected in the sample. Each cartridge contained approximately 0.2 grams of Tenax resin. A sample rate of approximately 0.1 Lpm through each Tenax tube was used. The flow rate through the Tenax cartridges was set prior to sample collection and checked after sample collection by placing a mass flow meter on the outlet of each Tenax tube and setting the position of the needle valve to achieve the desired flow rate.

The Tenax samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high resolution gas chromatographic separation and flame ionization detection (FID) of individual hydrocarbons for peak quantification, and/or combined mass spectrometric/Fourier transform infrared detection (MSD/FTIR), for peak identification. The resultant peaks were quantified and recorded by the chromatographic data systems.

Canisters. An integrated sample was collected in a canister using a pump and flow control device to maintain a constant sample flow rate into the canister over the entire sampling period. Canisters were used in order to quantify VOCs with a carbon number of 2 or more that are not found in the Tenax samples. The flow rate used is a function of the final desired sample pressure and the specified sampling period, for our purposes, 0.017 Lpm. Because the gas had already been diluted and cooled before sampling into the canister, liquid formation in the cans was not a concern.

For analysis, a known volume of gaseous sample is passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out C₂ and heavier VOC without trapping methane. The trap containing the condensed VOC is warmed with hot water and its contents injected into a gas chromatograph (GC) capillary column where separation of the VOC takes place. Detection of the hydrocarbons and oxygenated hydrocarbons is by FID while detection of the halogenated compounds is by electron capture detection (ECD), and the resultant peaks are quantified and recorded by an electronic integrator and by the chromatographic data system

Semivolatile Organic Compounds

Samples were collected using a filter followed by an adsorbent cartridge. The media used for collecting SVOCs were as follows:

- Pallflex (Putnam, CT) T60A20 102-mm TIGF filters;
- PUF sheets, purchased from E.R. Carpenter Company, Inc. (Richmond, VA) and cut into 2-inch diameter plugs;
- XAD-4 resin (20-60 mesh) purchased from Aldrich Chemical Company, Inc.

The sample was transferred from the sampling manifold through a 3/8-inch copper manifold leading to a momentum diffuser chamber followed by the filter and cartridge holder. The flow through the sampler was monitored continuously by a calibrated rotameter and kept at a target flow rate of 113 Lpm.

SVOCs were analyzed following procedures outlined in EPA Method TO-13. The samples were isotopically spiked, extracted in dichloromethane, and concentrated prior to analysis. Sample extracts were analyzed by the electron impact (EI) gas chromatography/mass spectrometric (GC/MS) technique, using a Hewlett-Packard 5890 GC equipped with a model 7673A Automatic Sampler and interfaced to a model 5970B Mass Selective Detector (MSD). To assist in the unique identification of individual compounds, selected samples were analyzed by combined gas chromatography/Fourier transform infrared/mass spectrometry (GC/IRD/MSD) technique, i.e., using the Fourier transform infrared detector to aid mass spectrometric identification. Quantification of polycyclic aromatic hydrocarbons (PAH), and other compounds of interest, was obtained by multiple ion detection (MID).

Carbonyls (Aldehydes and Ketones)

Carbonyls in air were collected by drawing sample through a cartridge impregnated with acidified DNPH, following procedures outlined in EPA Method TO-11A. The resulting products (hydrazones) in the cartridge are measured in the laboratory using high performance liquid chromatography (HPLC) to determine the levels of the carbonyl compounds originally present in

sample gas. Typically C₁-C₆ carbonyl compounds, including benzaldehyde, are measured effectively by this technique. The target flow rate used for this sample was 0.4 Lpm.

Sulfur dioxide

Filter packs containing a quartz filter followed by a potassium carbonate impregnated cellulose-fiber filters were used to collect SO₂ gas downstream of the dilution sampler. The target flow rate used for this sample was 160 scfh. These filters were extracted with hydrogen peroxide and then analyzed using IC.

Ammonia

Filter packs containing a quartz filter followed by a citric acid impregnated cellulose-fiber filter were used to collect ammonia gas downstream of the dilution sampler. The target flow rate used for this sample was 160 scfh. These filters were extracted with DI water and then analyzed using automated colorimetry.

Section 4

TEST RESULTS

All stack emission results are presented in units of milligrams per dry standard cubic meter (mg/dscm) and pounds per hour (lb/hr). Concentrations are corrected to a standard temperature of 68°F and a standard pressure of 29.92 inches of mercury unless otherwise indicated. See the conversion factors presented in Appendix B to convert to Système Internationale (SI) units. Substances that were undetected in any of the four test runs generally are not listed on the tables. Where shown, undetected data are flagged “ND”, treated as zeroes in sums, and excluded from average calculations. Data with one or more, but not all, constituents less than the detection limit are flagged with a “<” symbol. The approximate minimum in-stack detection limits achieved for all measured substances are given in Table 4-1. These detection limits are calculated from the analytical detection limits, an average sample volume and an average dilution ratio.

PROCESS OPERATING CONDITIONS

Heater operating conditions during testing are summarized in Table 4-2. The process heater operated at close to its normal firing rate corresponding to approximately 90 percent of full firing capacity.

The average fuel higher heating value (HHV) during each test was obtained from the fuel flow rate reported by the plant process data. The average heat input to the process heater during the test is the product of the average fuel-gas flow rate and the average fuel HHV. The average heat input was used to convert in-stack emission rates pounds per hour (lb/hr) to emission factors pounds of pollutant per million (lb/MMBtu), which are presented in Section 5. Results of the analysis of the fuel gas, as determined from grab samples taken during each run, are presented in Table 4-3. The difference in heating value between the plant data and grab samples is an indication of the variability of the process as the plant data is an average over the entire run and the grab sample is an instantaneous snapshot. Total reduced sulfur content of the fuel (as hydrogen sulfide (H₂S)) was approximately 200 parts per million by volume (ppmv) on average, with H₂S comprising only 2.8 ppmv (Table 4-4).

Table 4-1. Approximate In-Stack Detection Limits Achieved for Gas-Fired Process Heater Tests (Site Alpha).

Substance	Dilution Tunnel mg/dscm	In-stack methods mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm	Substance	Dilution Tunnel mg/dscm
Total PM mass	--	2.8E-01	Sn	3.0E-04	C-trimethylnaphthalene	1.5E-05	Anthracene	0.0E+00
PM10 mass	--	2.8E-01	Sr	1.9E-05	2-ethyl-1-methylnaphthalene	3.2E-04	9-methylantracene	8.8E-05
PM2.5 mass	1.3E-03	2.8E-01	Ti	5.0E-05	E-trimethylnaphthalene	1.9E-06	Fluoranthene	3.8E-06
Ag	2.1E-04	--	Tl	4.3E-05	F-trimethylnaphthalene	1.8E-06	Pyrene	7.6E-06
Al	1.7E-04	--	U	4.0E-05	2,3,5+I-trimethylnaphthalene	5.7E-06	9-Anthraldehyde	5.1E-05
As	2.8E-05	--	V	4.3E-05	2,4,5-trimethylnaphthalene	1.5E-05	Retene	1.1E-04
Au	5.4E-05	--	Y	2.3E-05	J-trimethylnaphthalene	1.5E-05	Benzonaphthothiophene	3.8E-06
Ba	9.0E-04	--	Zn	1.9E-05	1,4,5-trimethylnaphthalene	1.8E-04	1-MeFl+C-MePy/Fl	3.0E-05
Br	1.7E-05	--	Zr	3.0E-05	Acenaphthylene	2.0E-04	A-MePy/MeFl	1.9E-06
Ca	7.8E-05	--	SO4=	2.0E-03	Acenaphthene	5.0E-05	B-MePy/MeFl	1.9E-06
Cd	2.1E-04	--	NO3-	2.0E-03	Fluorene	2.3E-04	C-MePy/MeFl	1.9E-06
Cl	1.7E-04	--	NH4+	2.0E-03	Phenanthrene	1.5E-05	D-MePy/MeFl	1.9E-06
Co	1.5E-05	--	Cl-	2.0E-03	A-methylfluorene	2.0E-04	4-methylpyrene	3.8E-06
Cr	3.3E-05	--	NH3	5.3E-04	1-methylfluorene	1.3E-04	1-methylpyrene	1.5E-05
Cu	1.9E-05	--	SO2	1.3E-03	B-methylfluorene	1.3E-04	Benzo(c)phenanthrene	2.1E-05
Fe	2.6E-05	--	OC	1.5E-02	9-fluorenone	2.5E-04	Benz(a)anthracene	1.1E-05
Ga	3.3E-05	--	EC	3.4E-03	Xanthone	7.6E-06	7-methylbenz(a)anthracene	1.2E-05
Hg	4.5E-05	--	Naphthalene	1.8E-03	Acenaphthenequinone	1.1E-05	Chrysene	3.8E-06
In	2.3E-04	--	2-methylnaphthalene	1.2E-04	Perinaphthenone	1.9E-03	Benzanthrone	1.7E-05
K	1.1E-04	--	1-methylnaphthalene	7.2E-05	A-methylphenanthrene	9.1E-05	Benzo(a)anthracene-7,12-dione	7.0E-05
La	1.1E-03	--	Biphenyl	1.3E-04	2-methylphenanthrene	3.8E-06	5+6-methylchrysene	0.0E+00
Mg	0.0E+00	--	1+2-ethylnaphthalene	2.4E-04	B-methylphenanthrene	2.1E-05	Benzo(b+j+k)fluoranthene	1.9E-06
Mn	2.8E-05	--	2,6+2,7-dimethylnaphthalene	2.0E-04	C-methylphenanthrene	5.3E-05	7-methylbenzo(a)pyrene	1.3E-05
Mo	4.7E-05	--	1,3+1,6+1,7-dimethylnaphthalene	4.3E-04	1-methylphenanthrene	4.2E-05	Benzo(e)pyrene	1.2E-05
Na	0.0E+00	--	1,4+1,5+2,3-dimethylnaphthalene	1.9E-04	Anthrone	1.9E-06	Perylene	3.8E-06
Ni	1.5E-05	--	1,2-dimethylnaphthalene	1.3E-04	Anthraquinone	1.0E-04	Benzo(a)pyrene	1.1E-05
P	9.7E-05	--	2-Methylbiphenyl	3.0E-04	2,3-Benzofluorene	1.3E-05	Indeno[123-cd]pyrene	1.1E-05
Pb	5.2E-05	--	3-Methylbiphenyl	4.3E-04	3,6-dimethylphenanthrene	9.0E-05	Benzo(ghi)perylene	1.1E-05
Pd	1.9E-04	--	4-Methylbiphenyl	3.6E-05	A-dimethylphenanthrene	9.0E-05	Dibenzo(ah+ac)anthracene	1.1E-05
Rb	1.7E-05	--	Dibenzofuran	1.2E-04	B-dimethylphenanthrene	6.3E-05	Coronene	1.1E-05
S	8.7E-05	--	Bibenzyl	4.7E-03	C-dimethylphenanthrene	6.3E-05	Volatile Organic Compounds	1.1E-03
Sb	3.1E-04	--	A-trimethylnaphthalene	3.6E-06	1,7-dimethylphenanthrene	6.3E-05	Formaldehyde	3.4E-03
Se	2.1E-05	--	1-ethyl-2-methylnaphthalene	3.8E-06	D-dimethylphenanthrene	5.7E-05	Acetaldehyde	3.4E-03
Si	1.1E-04	--	B-trimethylnaphthalene	1.9E-06	E-dimethylphenanthrene	2.9E-05	Glyoxal	9.0E-04

Table 4-2. Process Operating Conditions (Site Alpha).

Parameter	Units	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01
Total fuel gas flow	scfh	129,474	135,448	136,267	143,685
Heater A feed rate	bph	1393	1301	1384	1404
Heater B feed rate	bph	2016	2402	2402	2402
Heater A outlet temperature	°F	695	705	695	700
Heater B outlet temperature	°F	658	712	909	716
Heater B firebox temperature	°F	1480	1484	1466	1476
Fuel heat content (HHV)	Btu/ft ³	1218	1231	1185	1168
Fuel specific gravity	--	0.80	0.77	0.78	0.76
O ₂	%	8.9	8.6	8.9	8.2
CO	ppm	0.5	1.0	0.5	21
NO _x	ppm	77	93	85	83
Heat Input (1)	MMBtu/hr	158	167	161	168

(1) Calculated from the fuel heat content and the fuel flow rate.

Table 4-3. Fuel Gas Analysis (Site Alpha).

Date	Units	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01	Average	RSD (%)
Specific Gravity	None	0.847	0.923	0.825	0.837	0.858	5.2
Gross Btu	Btu/cu. ft.	1294	1368	1252	1276	1298	3.9
Dry F Factor ¹	sdcf/MMBtu	7740	7640	7760	7669	7702	0.7

Methane	wt. %	39.1	30.2	41.3	37.2	37.0	13.0
Ethane	wt. %	9.7	9.7	9.9	9.8	9.8	1.0
Ethylene	wt. %	3.5	3.4	3.7	3.4	3.5	4.0
Propane	wt. %	10.0	8.8	4.5	8.9	8.1	30.2
Propylene	wt. %	2.9	5.5	6.0	4.4	4.7	29.2
i-Butane	wt. %	1.3	3.3	1.3	1.1	1.8	59.3
n-Butane	wt. %	5.4	4.8	4.9	4.7	5.0	6.3
1-Butene	wt. %	0.2	0.6	0.2	0.2	0.3	66.7
2-Methyl Butane	wt. %	ND	0.9	0.2	0.2	0.4	93.3
i-Pentane	wt. %	1.0	1.9	0.9	0.9	1.2	41.3
n-Pentane	wt. %	0.5	0.8	0.5	0.5	0.6	26.1
1-Pentene	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
2,2-Dimethyl Butane	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
2,3-Deimethyl Butane	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
2-Methyl Pentane	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
3-Methyl Pentane	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
n-Hexane	wt. %	0.1	0.1	0.1	0.1	0.1	0.0
1-Hexene	wt. %	ND	0.1	0.1	0.1	0.1	0.0
C ₆ +	wt. %	0.1	0.0	0.1	0.1	0.1	66.7
CO ₂	wt. %	0.2	0.1	0.2	0.1	0.2	38.5
CO	wt. %	0.5	0.5	0.5	0.6	0.5	9.5
O ₂	wt. %	1.8	2.2	1.8	1.6	1.9	13.6
N ₂	wt. %	7.5	8.9	8.0	8.1	8.1	7.1
H ₂	wt. %	15.9	17.7	15.3	17.4	16.6	7.0
H ₂ S	wt. %	<0.1	<0.1	<0.1	<0.1	<0.1	0.0

Total 100 100 100 100 100

(1) Dry F Factor at 68 F and 1 atm (ASTM 3588).

Table 4-4. Fuel Gas Sulfur Speciation Results, in ppmv (Site Alpha).

Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01	Average	RSD (%)
Time	14:37	16:52	13:10	12:30		
H ₂ S	2.5	2.3	3.1	3.4	2.8	18
Carbonyl Sulfide	12.6	15.5	12.3	13.4	13.5	11
Methyl Mercaptan	67	138	76.2	67.6	87.2	39
Ethyl Mercaptan	23.8	35.6	30.6	27.8	29.5	17
Unidentified Sulfur Compounds	60.8	73.8	65.5	61.4	65.4	9
Total Reduced Sulfur as H ₂ S	167	265.3	188	174	199	23

PRELIMINARY TEST RESULTS

Preliminary tests were conducted to establish a single point in the stack for sample collection. A velocity profile was developed by traversing the stack with the pitot probe before and after each test. The resulting average velocity profile was used to correct the velocities measured at the center during sampling to the overall stack average velocity.

STACK GAS CONDITIONS AND FLOW RATE

A summary of the stack conditions during testing is presented in Table 4-5. Stack gas temperature during the tests averaged 771-807°F.

Table 4-5. Average Stack Conditions (Site Alpha).

Parameter	Units	Run 1	Run 2	Run 3	Run 4
Date		15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01
Stack Temperature	°F	771	807	798	806
Moisture	%v	11	11	11	12
Velocity	ft/s	26	26	26	25
	m/s	8.0	7.9	8.0	7.5
Flow Rate	acfm	150,900	148,600	150,600	141,800
	dscfm	57,800	55,300	56,600	52,000
	dscmm	1,640	1,570	1,600	1,470

IN-STACK AND IMPINGER METHOD RESULTS

Particulate Mass

FPM. FPM results as measured by Method PRE-4 are presented in Table 4-6. Total FPM, which includes all PM collected in the in-stack nozzle/cyclone assembly and on the in-stack filter, ranged from 0.17 to 1.01 mg/dscm. FPM less than 10 micrometers, which includes the

portion of total FPM collected downstream of the PM10 cyclone, was 0.17 to 0.69 mg/dscm. FPM less than 2.5 micrometers, which includes the portion of FPM collected downstream of the PM2.5 cyclone and on the in-stack filter, was 0.12 to 0.49 mg/dscm. These in-stack concentrations correspond to total weight gains in the sampling train of 0.7 to 4 milligrams (mg), with uncorrected net weights in each fraction of –1.6 to 1.7 mg.

Table 4-6. Filterable Particulate Matter Results (Site Alpha).

Parameter	Units	Results					
Run Number	-	1	2	3	4	Average	RSD
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		
Total FPM	mg/dscm	0.68	< 1.01	< 0.17	0.99	< 0.71	55%
(by Method PRE-4)	lb/hr	0.15	< 0.21	< 0.04	0.19	< 0.15	54%
Total FPM	mg/dscm	< 0.39	0.38	< 0.56	< 0.40	< 0.43	19%
(by Method 17)	lb/hr	< 0.08	0.08	< 0.12	< 0.08	< 0.09	21%
FPM <10 µm	mg/dscm	0.49	< 0.54	< 0.17	0.68	< 0.47	46%
(by Method PRE-4)	lb/hr	0.11	< 0.11	< 0.04	0.13	< 0.10	44%
FPM <2.5 µm	mg/dscm	0.49	< 0.38	< 0.12	0.38	< 0.34	46%
(by Method PRE-4)	lb/hr	0.11	< 0.08	< 0.02	0.07	< 0.07	48%

<-one or more, but not all, constituents are less than the detection limit

RSD-relative standard deviation

Acetone reagent blanks were significant relative to some samples. Acetone blank corrections ranged from 5 to 95 percent of the acetone rinse net weights. These results reflect the extremely low PM loading in the stack and suggest that the mass loading on the filters may be at or below the practical limits of the overall method.

Total FPM as measured by Method 17 is also shown in Table 4-6. The total FPM as measured by the two different methods is on the same order of magnitude.

CPM. There has been much comment on the effect of a post-test nitrogen purge on the levels of CPM collected in the Method 202 impingers. To investigate the impact of the purge two separate trains were sampled simultaneously, as described in Section 3, with one being purged after sampling was completed and the other not undergoing a purge. The results are summarized in Table 4-7.

Table 4-7. Condensable Particulate Matter (Method 202) Results (Site Alpha).

Parameter	Units						
Run Number	-	1	2	3	4	Average	RSD
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		
Inorganic CPM (Purged Train) (1)	mg/dscm	2.5E+1	1.2E+1	1.4E+1	1.9E+1	1.7E+1	34%
Inorganic CPM (Unpurged Train)	mg/dscm	7.5E+0	8.4E-1	7.3E+0	4.9E+0	5.1E+0	60%
Organic CPM (Purged Train)	mg/dscm	1.1E+0	1.1E+0	1.7E+0	1.2E+0	1.3E+0	24%
Organic CPM (Unpurged Train)	mg/dscm	1.3E+0	5.1E-1	8.9E-1	5.5E-1	8.2E-1	46%
Sulfate (as SO ₄ ⁼) in Impingers (Purged Train)	mg/dscm	1.9E+1	1.1E+1	1.1E+1	1.5E+1	1.4E+1	28%
Sulfate (as SO ₄ ⁼) in Impingers (Unpurged Train)	mg/dscm	5.8E+0	3.0E+0	5.8E+0	4.4E+0	4.7E+0	29%
Total CPM (Purged Train)	mg/dscm	2.6E+1	1.3E+1	1.5E+1	2.0E+1	1.9E+1	32%
Total CPM (Unpurged Train)	mg/dscm	8.8E+0	1.3E+0	8.4E+0	5.5E+0	6.0E+0	57%
Inorganic CPM (Purged Train) (1)	lb/hr	5.4E+0	2.5E+0	2.9E+0	3.7E+0	3.6E+0	36%
Inorganic CPM (Unpurged Train)	lb/hr	1.6E+0	1.7E-1	1.5E+0	9.5E-1	1.1E+0	62%
Organic CPM (Purged Train)	lb/hr	2.3E-1	2.2E-1	3.6E-1	2.4E-1	2.6E-1	26%
Organic CPM (Unpurged Train)	lb/hr	2.9E-1	1.0E-1	1.9E-1	1.1E-1	1.7E-1	50%
Sulfate (as SO ₄ ⁼) in Impingers (Purged Train)	lb/hr	4.1E+0	2.2E+0	2.2E+0	3.0E+0	2.9E+0	30%
Sulfate (as SO ₄ ⁼) in Impingers (Unpurged Train)	lb/hr	1.3E+0	6.1E-1	1.2E+0	8.5E-1	9.8E-1	31%
Total CPM (Purged Train)	lb/hr	5.7E+0	2.7E+0	3.3E+0	4.0E+0	3.9E+0	34%
Total CPM (Unpurged Train)	lb/hr	1.9E+0	2.8E-1	1.8E+0	1.1E+0	1.3E+0	60%

RSD-relative standard deviation

CPM-condensable particulate matter

(1) Purged Train: one-hour post-test nitrogen purge performed; Unpurged Train: no purge performed.

Purged Train. The average total CPM, which is the sum of the evaporated organic extract, the inorganic residue (corrected for addition of NH₄OH and water reagent blank) and the back-half filter, is 18.9 mg/dscm. The reagent blanks were not significant relative to the sample masses; the water reagent blank ranged from 4 to 8% percent of the uncorrected net weights and the dichloromethane blank was below detection limits. The total inorganic mass is 17.4 mg/dscm, 80 percent of which is accounted for by sulfate, with a concentration of 13.9 mg/dscm. This sulfate concentration is determined from the aliquot taken from the impinger catch and rinse before it is extracted with the organic solvent. The average organic CPM concentration is 1.3 mg/dscm. This result is higher than previous tests on a gas-fired boiler, gas-fired heater and gas-fired steam generator that had organic CPM concentrations of 0.6, 0.2 and 0.8 mg/dscm, respectively.

CPM concentration was approximately 50 times greater than FPM2.5 on average. On average, approximately 92 percent of the CPM was found in the inorganic fraction, while 7 percent was found in the organic fraction; the remaining mass is accounted for in the

impinger filter that is not speciated. The inorganic and organic CPM results are somewhat variable from run to run, with standard deviations equal to 34 and 24 percent of the average result, respectively. CPM results have been corrected for dichloromethane and water recovery blank results. The data are also corrected for ammonium ion retained and combined water released in the acid base titration, as described in Method 202. Further discussion of the data is provided in Section 7.

Unpurged Train. The average total CPM concentration is 6.0 mg/dscm and the average inorganic CPM concentration is 5.1 mg/dscm, both approximately three times lower than that determined from the Purged Train. The average organic CPM is 0.8 mg/dscm, which is similar to that obtained in the purged train. This result is expected since the purge is meant to only affect the inorganic CPM catch. The relative proportions of the CPM constituents are fairly consistent between the two trains, however. Ninety-two percent of the inorganic CPM is accounted for by the sulfate, with an average concentration of 4.7 mg/dscm. Eighty-five percent of the CPM is found in the inorganic fraction and 13 percent in the organic fraction (the remaining mass is accounted for by the back-half filter and is not characterized).

It was expected that the purged train would show lower CPM and sulfate levels, however the reverse is indicated by the results. Further investigation of the potential causes of these anomalous results indicates that the use of a different gasket material used in the in-stack filter of the PRE-4 train may have contributed to the elevated CPM levels in the purged train. Due to the higher stack temperatures, the Teflon[®] and Viton gaskets could not be used, so a graphite-impregnated material was used for the first run only, after which it was discovered that it had disintegrated during the run. For subsequent runs, a metal gasket was used in conjunction with copper heat tape to improve the seal. Another possible source of bias is the use of stainless steel probes instead of a glass-lined probe. Stainless steel is known to be more reactive with CO at higher temperatures, so it is possible that at the high stack temperatures, the stainless steel acted as a catalyst to oxidize the sulfur dioxide and form sulfate.

Additionally, the resuspended inorganic residues of the two trains were analyzed for a broader range of elements and ions in order to more fully speciate the inorganic CPM. These results are presented in Table 4-8. Sulfate, ammonium, sodium and calcium are the four most abundant compounds in the inorganic CPM fraction for both trains.

Purged Train. SO_4^- , NH_4^+ , Na and Ca account for an average of 18.7 mg/dscm, or 107 percent, of the inorganic CPM mass as presented in Table 4-8. The remaining 29 elements and ions that were detected account for an average of 0.2 mg/dscm, or 1 percent, of the average inorganic CPM mass.

Unpurged Train. SO_4^- , NH_4^+ , Na and Ca account for an average of 6.4 mg/dscm, which is approximately 125 percent of the inorganic CPM mass as presented in Table 4-8. The remaining constituents account for an additional 4 percent.

Although the results do not match expected behavior, the additional analysis confirms that SO_4^- is the dominant compound in the inorganic residue. Ammonium is also present in significant amounts (ammonium hydroxide is added during sample analysis). It is believed the majority of SO_4^- , found in the impinger contents is an artifact resulting from gaseous SO_2 in the stack gas. These results and issues are discussed in more detail in Section 7.

DILUTION SAMPLER RESULTS

Particulate Mass

PM2.5 mass measurements using the dilution sampler include both solid aerosols that are directly emitted and those that condense under simulated stack plume conditions in the residence chamber. The dilution sampler determines only the PM2.5 fraction of PM emissions; particles with an aerodynamic diameter larger than 2.5 micrometers in the stack and particles that grow to be larger than 2.5 micrometers in the dilution sampler are excluded. Results from these measurements show that PM2.5 concentrations and emission rates average 0.041 mg/dscm and 0.0086 lb/hr, respectively, with a relative standard deviation of 15 percent, based on TMF weight (Table 4-9). These results are almost three orders of magnitude lower than the sum of FPM2.5 and CPM measured by EPA Methods PRE-4 and 202.

Table 4-8. Speciation (mg/dscm) of Back-Half Impinger Catch (Site Alpha).

	Run 1 (mg/dscm)		Run 2 (mg/dscm)		Run 3 (mg/dscm)		Run 4 (mg/dscm)		Average (mg/dscm)	
	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged	Purged	Unpurged
Sulfate	1.87E+1	5.78E+0	1.07E+1	2.96E+0	1.06E+1	5.76E+0	1.52E+1	4.38E+0	1.4E+01	4.7E+00
Ammonium	6.15E+0	1.71E+0	3.57E+0	3.80E-1	3.30E+0	1.64E+0	4.84E+0	1.18E+0	4.5E+00	1.2E+00
Na	3.08E-1	3.37E-1	2.38E-1	2.32E-1	2.83E-1	3.33E-1	3.14E-1	3.50E-1	2.9E-01	3.1E-01
Ca	1.43E-1	1.35E-1	6.19E-2	7.82E-2	1.15E-1	1.09E-1	8.47E-2	1.34E-1	1.0E-01	1.1E-01
Fe	1.65E-2	5.06E-2	6.90E-2	7.18E-3	9.42E-2	2.44E-1	1.43E-1	1.42E-2	8.1E-02	7.9E-02
K	< 3.08E-2	3.37E-2	3.10E-2	2.96E-2	< 2.59E-2	2.66E-2	3.87E-2	< 2.41E-2	< 3.2E-02	2.9E-02
Al	1.79E-2	2.12E-2	1.69E-2	1.10E-2	2.83E-2	3.55E-2	2.66E-2	1.03E-2	2.2E-02	1.9E-02
Mg	1.93E-2	2.65E-2	8.81E-3	9.51E-3	2.05E-2	1.49E-2	1.26E-2	1.45E-2	1.5E-02	1.6E-02
Ni	1.82E-3	9.88E-3	1.12E-2	< 4.65E-4	1.48E-2	6.43E-2	2.66E-2	1.20E-3	1.4E-02	< 1.9E-02
Cr	3.08E-4	2.65E-3	9.76E-3	2.75E-4	1.15E-2	2.88E-2	2.66E-2	1.69E-3	1.2E-02	8.4E-03
Si	< 3.08E-3	5.54E-3	7.38E-3	< 2.32E-3	9.90E-3	4.66E-3	2.37E-2	4.82E-3	< 1.1E-02	< 4.3E-03
Fluoride	< 6.99E-3	6.03E-3	6.67E-3	7.82E-3	9.66E-3	1.35E-2	< 6.05E-3	3.07E-3	< 7.3E-03	7.6E-03
Zn	1.04E-2	8.92E-3	6.67E-3	1.31E-3	6.60E-3	6.65E-3	4.11E-3	3.07E-3	6.9E-03	5.0E-03
Chloride	< 6.99E-3	1.61E-2	< 5.95E-3	6.13E-3	< 5.89E-3	ND	< 6.05E-3	ND	< 6.2E-03	< 1.1E-02
Mn	6.43E-3	1.40E-1	5.48E-3	4.01E-4	8.01E-3	6.21E-2	1.91E-3	7.88E-4	5.5E-03	5.1E-02
B	3.36E-3	3.37E-3	5.24E-3	3.17E-4	8.01E-3	4.88E-3	4.84E-3	9.42E-4	5.4E-03	2.4E-03
Nitrate (as N)	4.48E-3	3.86E-3	ND	3.38E-3	3.53E-3	3.55E-3	3.87E-3	3.29E-3	< 4.0E-03	3.5E-03
Cu	4.48E-3	4.34E-3	9.05E-4	4.01E-4	1.70E-3	1.53E-2	1.69E-3	7.23E-4	2.2E-03	5.2E-03
Mo	< 1.54E-4	2.39E-4	1.12E-3	< 1.16E-4	1.25E-3	1.80E-3	4.11E-3	3.50E-4	< 1.7E-03	< 6.3E-04
P	< 1.85E-3	5.06E-3	< 1.57E-3	< 1.39E-3	< 1.55E-3	1.46E-3	< 1.60E-3	< 1.45E-3	< 1.6E-03	< 2.3E-03
Tl	< 1.85E-3	< 1.59E-3	< 1.57E-3	< 1.39E-3	< 1.55E-3	< 1.46E-3	< 1.60E-3	< 1.45E-3	< 1.6E-03	< 1.5E-03
Sn	< 1.54E-3	< 1.33E-3	< 1.31E-3	< 1.16E-3	< 1.30E-3	< 1.22E-3	< 1.33E-3	< 1.20E-3	< 1.4E-03	< 1.2E-03
Pb	< 6.15E-4	< 5.30E-4	< 5.24E-4	6.55E-4	< 5.18E-4	< 4.88E-4	< 5.32E-4	< 4.82E-4	< 5.5E-04	< 5.4E-04
Sr	4.76E-4	1.18E-3	3.33E-4	3.38E-4	6.13E-4	8.20E-4	6.05E-4	7.45E-4	5.1E-04	7.7E-04
Co	< 3.08E-4	2.41E-3	2.62E-4	< 2.32E-4	3.06E-4	1.37E-3	5.08E-4	< 2.41E-4	< 3.5E-04	< 1.1E-03
Ti	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	3.55E-4	3.87E-4	3.29E-4	< 3.0E-04	< 3.0E-04
Ag	< 3.08E-4	7.71E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	5.10E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 4.4E-04
V	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	< 2.44E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 2.5E-04
Zr	< 3.08E-4	< 2.65E-4	< 2.62E-4	< 2.32E-4	< 2.59E-4	< 2.44E-4	< 2.66E-4	< 2.41E-4	< 2.7E-04	< 2.5E-04
Cd	8.11E-4	2.05E-4	5.71E-5	< 4.65E-5	7.54E-5	1.22E-3	< 5.32E-5	9.64E-5	2.5E-04	< 3.9E-04
Ba	1.40E-4	1.11E-3	1.50E-4	2.75E-4	1.48E-4	3.10E-4	1.69E-4	3.07E-4	1.5E-04	5.0E-04
Be	< 3.08E-5	< 2.65E-5	< 2.62E-5	< 2.32E-5	< 2.59E-5	< 2.44E-5	< 2.66E-5	< 2.41E-5	< 2.7E-05	< 2.5E-05

< - one or two runs is below limit of quantitation (Detection limit x 3.33)

n/a-not applicable; two or more runs not detected

ND-not detected

Table 4-9. Dilution Sampler PM2.5 Results (Site Alpha).

	Units	Results						
Run Number	-	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		(%)	22-Feb-01
PM2.5	mg/dscm	3.66E-2	4.81E-2	ND	3.89E-2	< 4.12E-2	15	3.08E-2
	lb/hr	7.94E-3	1.02E-2	ND	7.57E-3	< 8.58E-3	17	n/a

The gravimetric result for Run 3 was marked as suspect by the analytical lab, due to the indication of zero net weight gain even though a light, visible deposit was observed on the filter.

The PM2.5 concentration measured in the process heater stack gas was approximately equal to the concentration measured in the ambient air. The annual (2001) average for PM2.5 obtained from local air quality management district ambient monitoring data was 0.021 mg/dscm, with a maximum 24-hour concentration of 0.073 mg/dscm, indicating that the PM loading collected by the single ambient sample during this test is within the expected range. The comparability of the average mass collected on the sample filters with that from the ambient sample suggests that the majority of the PM being measured in the stack is coming from the ambient air used during combustion rather than from combustion itself.

The concentration of PM2.5 using the dilution sampler is an order of magnitude lower than filterable PM2.5 measured using Method PRE-4 and almost three orders of magnitude lower than CPM measured using Method 202. CPM is normally included in regulatory definitions of PM10. These emission measurements are strongly method dependent because the dilution sampler replicates conditions experienced by the stack emissions as they mix with the atmosphere more accurately than Method 202. Due to suspected artifacts associated with Method 202, it is believed the dilution sampler results are more representative of the true primary PM2.5 emissions.

Sulfate, Nitrate, Chloride, Ammonium and Soluble Sodium

Quartz filters were analyzed for $\text{SO}_4^{=}$, Cl^- , NO_3^- , NH_4^+ , and Na^+ ion. Of these, $\text{SO}_4^{=}$ had the highest average concentration at 0.029 mg/dscm, followed by NH_4^+ at 0.014 mg/dscm (Table 4-10). All ions in the field blank except Na^+ were present below detectable levels; Na^+

concentration in the field blank was comparable to the average sample concentration (please refer to Section 6 for further discussion of blanks and ambient samples).

Table 4-10. Dilution Sampler Ion Results (Site Alpha).

Parameter	Units	Value						
Run Number	-	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		(%)	22-Feb-01
Sulfate	mg/dscm	1.77E-2	3.42E-2	1.39E-2	4.96E-2	2.88E-2	57	1.35E-03
	lb/hr	3.83E-3	7.27E-3	2.95E-3	9.65E-3	5.92E-3	52	n/a
Nitrate	mg/dscm	5.72E-3	1.14E-2	5.24E-3	4.67E-3	6.76E-3	46	5.64E-04
	lb/hr	1.24E-3	2.43E-3	1.11E-3	9.09E-4	1.42E-3	48	n/a
Chloride	mg/dscm	ND	ND	2.36E-3	2.69E-3	< 2.53E-3	9	1.90E-03
	lb/hr	ND	ND	5.00E-4	5.24E-4	< 5.12E-4	3	n/a
Ammonium	mg/dscm	ND	1.51E-2	6.34E-3	1.93E-2	< 1.36E-2	49	2.92E-04
	lb/hr	ND	3.22E-3	1.35E-3	3.76E-3	< 2.78E-3	46	n/a
Soluble Na	mg/dscm	3.35E-4	2.13E-4	2.60E-4	2.57E-4	2.66E-4	19	6.60E-05
	lb/hr	7.27E-5	4.52E-5	5.51E-5	5.01E-5	5.58E-5	21	n/a

n/a - not applicable

ND - not detected

RSD- Relative standard deviation

The quartz filters used for these measurements have the potential for a positive $\text{SO}_4^{=}$ bias due to their high surface area providing the potential for adsorptive artifacts. The average $\text{SO}_4^{=}$ is 2.6 times higher than the elemental S content on the TMF (see later discussion), which is in very good agreement with the expected value of 3.0 based on the ratio of molecular weights, indicating that any bias due to SO_2 adsorption is not significant. The average $\text{SO}_4^{=}$ concentration from the dilution sampler is more than 3 orders of magnitude lower than the average concentration reported above for Method 202. This difference lends further support to the possibility of a significant sampling artifact in Method 202 due to gaseous SO_2 in the stack gas. Chloride was detected in the ambient sample at a level comparable to that in the field samples (please refer to Section 6 for further discussion of blanks and ambient samples).

OC, EC and Organic Species

OC and EC were measured on quartz fiber filters from the dilution sampler as a measurement of particulate carbon emissions including the organic compounds that condense under ambient conditions. OC concentrations ranged from 0.069 to 0.078 mg/dscm; EC ranged from 0.0039 to 0.014 mg/dscm (Table 4-11). OC accounts for approximately 90 percent of the total carbon mass. Elemental carbon was detected in the ambient sample at a level comparable to that in the

field samples. Organic and elemental carbon were below detection limits in the field blank (please refer to Section 6 for additional discussion of blank results and ambient samples).

Table 4-11. OC/EC as Measured by the Dilution Sampler (Site Alpha).

Parameter	Units	Value						
Run Number	-	Run 1	Run 2	Run 3	Run 4	Average*	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		(%)	22-Feb-01
Organic Carbon (OC) **	mg/dscm	7.76E-2	6.95E-2	6.89E-2	7.28E-2	7.22E-2	6	3.57E-3
	lb/hr	1.68E-2	1.48E-2	1.46E-2	1.42E-2	1.51E-2	8	n/a
Elemental Carbon (EC)	mg/dscm	7.36E-3	6.95E-3	3.86E-3	1.41E-2	8.07E-3	54	7.88E-4
	lb/hr	1.60E-3	1.48E-3	8.20E-4	2.75E-3	1.66E-3	48	n/a
Total Carbon (TC)	mg/dscm	8.50E-2	7.65E-2	7.28E-2	8.70E-2	8.03E-2	8	4.36E-3
	lb/hr	1.84E-2	1.63E-2	1.54E-2	1.69E-2	1.68E-2	8	n/a
Backup Filter OC ***	mg/dscm	8.62E-2	5.40E-2	8.54E-2	7.77E-2	7.58E-2	20	1.72E-3
	lb/hr	1.87E-2	1.15E-2	1.81E-2	1.51E-2	1.59E-2	21	n/a

* TC Average calculated as average of TC runs, not OC Average + EC Average.

** OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote *** and Sections 6 & 7 for further discussion.

*** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter. Refer to Sections 6 & 7 for further discussion.

n/a- not applicable

ND - Not Detected

RSD- Relative Standard Deviation

The quartz fiber filters used for OC/EC analysis have the potential for positive OC bias due to adsorption of VOCs on the media and the collected sample. A backup quartz fiber filter placed directly behind the TMF was used to evaluate the potential magnitude of the absorptive bias on the clean media. The OC concentrations on the backup filter and on the primary filter are very similar; the average results are not significantly different at the 95 percent confidence level. Therefore the magnitude of any bias in the OC result is potentially significant, and may be on the same magnitude as the measured value. Supporting this observation is the fact that the average total PM_{2.5} mass is only about 25% of the average reconstructed mass (averages exclude run 3 which invalidated for PM), and on average OC comprises about 50 percent of the reconstructed mass, albeit with high uncertainty associated with all the measurements. The potential OC bias is the subject of ongoing studies, and because the bias is not well understood it is the current convention not to subtract the backup OC from the primary result. However, the similarity of the primary and backup OC results indicates the need for caution when using these results. Additional discussion of this bias is located in Section 7.

SVOCs. SVOCs were determined on the combined TIGF/PUF/XAD-4/PUF cartridge used with the dilution sampler. This method determines both particulate- and vapor-phase SVOCs together. Results of the stack emissions and ambient air sample are presented in Table 4-12. Naphthalene is the most abundant SVOC in the dilution method samples, with an average concentration of 0.0042 mg/dscm, but was only detected in one of four runs. All of the average SVOC stack gas concentrations are a factor of ten greater than the ambient air concentration. 1,3+1,6+1,7-dimethylnaphthalene, 2-ethyl-1-methylnaphthalene, and acenaphthylene are all present at significant levels in the sample, with average concentrations that are more than two standard deviations above their ambient concentrations, making them potential source apportionment marker species (please refer to further discussion in Sections 6 and 7).

Tenax. Only the reactions of VOCs with carbon numbers higher than seven are considered important in formation of secondary organic aerosols (Grosjean and Seinfeld, 1989), because the products from those having fewer than seven carbon atoms are too volatile to form aerosols under atmospheric conditions. Tenax sorbent was used to collect VOCs with a boiling point of approximately 40 °C and greater. Tenax tubes for Runs 2 and 4 were damaged during sampling and could not be analyzed.

Discussions with the organic lab indicate that the Tenax sample material is susceptible to degradation from components in the sample stream, making it difficult to differentiate true emissions from those due to Tenax decomposition. In light of this observation, the Tenax results should be viewed as highly uncertain, in particular for benzaldehyde, benzoic acid, hexadecanoic acid, phenol and acetophenone, which are all potential Tenax degradation products. After benzaldehyde and hexadecanoic acid (both potential Tenax degradation products) styrene was the most abundant VOC detected during sampling, with an average concentration of 0.092 mg/dscm (Table 4-13). In general, the average VOC concentration in the stack gas was within a factor of approximately ten to forty times the ambient air concentration. The loss of Runs 2 and 4, combined with the high uncertainty from the Tenax degradation products, makes it difficult to draw significant conclusions from the Tenax data. m&p-xylene, o-xylene, m-ethyltoluene, dodecane, 1,3-dichlorobenzene, C-dimethylindane, and tetradecane were the only VOCs detected in more than sample and had field blank and ambient sample concentrations less than the 95%

Table 4-12. Semi-Volatile Organic Compound (SVOC) Results (mg/dscm) (Site Alpha).

Parameter	Value							
Run Number Date	Run 1 15-Feb-01	Run 2 16-Feb-01	Run 3 20-Feb-01	Run 4 21-Feb-01	Average	RSD (%)	Ambient 22-Feb-01	MDL
Naphthalene	4.2E-3	ND	ND	ND	< 4.2E-3	n/a	ND	1.8E-3
2-methylnaphthalene	8.0E-3	2.9E-3	2.8E-3	2.0E-3	3.9E-3	70	7.8E-5	1.2E-4
1-methylnaphthalene	3.5E-3	1.3E-3	1.3E-3	9.5E-4	1.8E-3	67	3.7E-5	7.2E-5
Biphenyl	1.8E-4	ND	ND	ND	< 1.8E-4	n/a	ND	1.3E-4
1+2-ethylnaphthalene	6.7E-4	3.2E-4	3.9E-4	2.7E-4	4.1E-4	44	7.7E-6	2.4E-4
2,6+2,7-dimethylnaphthalene	1.1E-3	4.9E-4	6.0E-4	3.9E-4	6.5E-4	51	1.1E-5	2.0E-4
1,3+1,6+1,7-dimethylnaphthalene	1.9E-3	7.7E-4	1.1E-3	6.4E-4	1.1E-3	51	1.8E-5	4.3E-4
1,4+1,5+2,3-dimethylnaphthalene	4.0E-4	ND	2.5E-4	ND	< 3.2E-4	32	ND	1.9E-4
Dibenzofuran	ND	ND	ND	ND	ND	n/a	4.3E-6	1.2E-4
A-trimethylnaphthalene	3.5E-4	1.5E-4	2.0E-4	1.3E-4	2.1E-4	49	5.6E-6	3.6E-6
1-ethyl-2-methylnaphthalene	1.1E-4	5.9E-5	7.8E-5	6.6E-5	7.7E-5	27	1.8E-6	3.8E-6
B-trimethylnaphthalene	2.5E-4	1.2E-4	1.6E-4	1.2E-4	1.6E-4	40	4.1E-6	1.9E-6
C-trimethylnaphthalene	2.5E-4	1.2E-4	1.9E-4	1.6E-4	1.8E-4	31	4.4E-6	1.5E-5
2-ethyl-1-methylnaphthalene	1.1E-3	7.0E-4	ND	5.4E-4	< 7.9E-4	37	1.6E-5	3.2E-4
E-trimethylnaphthalene	1.0E-4	5.2E-5	9.5E-5	4.9E-5	7.4E-5	37	1.8E-6	1.9E-6
2,3,5+1-trimethylnaphthalene	1.8E-4	8.9E-5	1.3E-4	5.3E-5	1.1E-4	47	3.2E-6	5.7E-6
J-trimethylnaphthalene	4.7E-5	7.7E-5	1.1E-4	7.9E-5	7.7E-5	31	1.8E-6	1.5E-5
1,4,5-trimethylnaphthalene	ND	ND	ND	ND	ND	n/a	5.4E-6	1.8E-4
Acenaphthylene	2.4E-4	ND	2.5E-4	ND	< 2.5E-4	3	ND	2.0E-4
Phenanthrene	1.3E-4	5.8E-5	1.9E-4	6.5E-5	1.1E-4	55	4.0E-6	1.5E-5
9-fluorenone	ND	ND	2.7E-4	3.6E-4	< 3.1E-4	18	ND	2.5E-4
Xanthone	ND	ND	ND	ND	ND	n/a	7.7E-7	7.6E-6
2-methylphenanthrene	2.8E-5	2.4E-5	2.9E-5	1.1E-5	2.3E-5	37	3.7E-7	3.8E-6
Anthrone	1.1E-5	2.7E-6	3.6E-6	ND	< 5.7E-6	77	7.5E-8	1.9E-6
C-dimethylphenanthrene	1.6E-4	ND	2.6E-4	1.6E-4	< 1.9E-4	29	9.0E-6	6.3E-5
D-dimethylphenanthrene	6.4E-5	ND	ND	ND	< 6.4E-5	n/a	ND	5.7E-5
E-dimethylphenanthrene	8.9E-5	ND	ND	ND	< 8.9E-5	n/a	ND	2.9E-5
Anthracene	ND	ND	2.7E-6	ND	< 2.7E-6	n/a	ND	0.0E+0
Fluoranthene	2.0E-5	2.7E-5	4.1E-5	2.0E-5	2.7E-5	37	8.7E-7	3.8E-6
Pyrene	1.3E-5	ND	1.9E-5	ND	< 1.6E-5	24	4.0E-7	7.6E-6
Benzonaphthothiophene	ND	ND	ND	ND	ND	n/a	1.5E-7	3.8E-6
B-MePy/MeFl	ND	9.1E-6	ND	ND	< 9.1E-6	n/a	1.7E-7	1.9E-6
C-MePy/MeFl	8.0E-6	4.5E-6	1.4E-4	2.6E-5	4.4E-5	144	1.8E-6	1.9E-6
D-MePy/MeFl	4.5E-6	7.3E-6	4.3E-5	1.3E-5	1.7E-5	104	7.9E-7	1.9E-6
Benzo(c)phenanthrene	ND	ND	ND	ND	ND	n/a	8.2E-7	2.1E-5
Benz(a)anthracene	9.8E-5	1.3E-3	1.4E-4	9.4E-5	4.1E-4	146	1.2E-5	1.1E-5
7-methylbenz(a)anthracene	4.0E-5	2.2E-4	ND	3.3E-5	< 9.9E-5	109	4.4E-6	1.2E-5
Chrysene	2.0E-5	ND	1.4E-5	1.7E-5	< 1.7E-5	18	3.2E-7	3.8E-6
Benzanthrone	1.9E-5	ND	ND	ND	< 1.9E-5	n/a	8.2E-7	1.7E-5
5+6-methylchrysene	8.9E-6	6.3E-6	8.1E-6	1.1E-5	8.5E-6	21	3.5E-7	0.0E+0
7-methylbenzo(a)pyrene	ND	ND	ND	ND	ND	n/a	1.7E-6	1.3E-5
Benzo(e)pyrene	ND	ND	ND	5.1E-5	< 5.1E-5	n/a	ND	1.2E-5
Benzo(a)pyrene	1.5E-5	ND	ND	ND	< 1.5E-5	n/a	4.5E-7	1.1E-5
Indeno[123-cd]pyrene	ND	ND	ND	ND	ND	n/a	3.7E-7	1.1E-5

n/a- Not applicable. Only one run was within detectable limits.

ND - not detected

MDL - Method Detection Limit

Table 4-13. Volatile Organic Compound (VOC) Results from Tenax (Site Alpha).

Parameter	Value						
Units	mg/dscm					%	mg/dscm
Run Number	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			
Benzaldehyde	2.79E-1		1.63E-1		2.21E-1	37	3.91E-3
Hexadecanoic acid	2.99E-1		8.28E-2		1.91E-1	80	1.08E-2
Styrene	* 1.55E-1		2.79E-2		9.16E-2	98	7.51E-4
Acetophenone	1.06E-1		5.67E-2		8.12E-2	43	2.06E-3
Phenol	5.23E-2		2.49E-2		3.86E-2	50	8.22E-4
Nonanal	3.15E-2		9.72E-3		2.06E-2	75	3.28E-4
Decanal	ND		1.66E-2		< 1.66E-2	n/a	6.69E-4
m & p-xylene	1.33E-2		1.41E-2		1.37E-2	4	8.94E-4
Nonane	8.82E-3		6.81E-3		7.82E-3	18	2.79E-4
Ethylbenzene	7.75E-3		4.92E-3		6.33E-3	32	2.78E-4
m & p-methylphenol	* 6.05E-3		ND		< 6.05E-3	n/a	6.38E-5
Decane	7.09E-3		3.75E-3		5.42E-3	43	2.07E-4
Biphenyl	6.65E-3		3.52E-3		5.09E-3	43	1.03E-4
o-xylene	5.04E-3		4.72E-3		4.88E-3	5	3.08E-4
Heptanal	4.82E-3		ND		< 4.82E-3	n/a	ND
Undecane	5.01E-3		3.87E-3		4.44E-3	18	2.58E-4
Dodecene	2.77E-3		5.77E-3		4.27E-3	50	1.70E-4
1,2,4-trimethylbenzene	2.33E-3		4.37E-3		3.35E-3	43	2.67E-4
m-ethyltoluene	3.40E-3		3.25E-3		3.33E-3	3	1.86E-4
1-undecene	4.35E-3		2.05E-3		3.20E-3	51	7.78E-5
Naphthalene	3.78E-3		2.25E-3		3.01E-3	36	8.38E-5
Dodecane	3.31E-3		2.67E-3		2.99E-3	15	1.87E-4
1-nonene	2.87E-3		2.40E-3		2.63E-3	13	9.58E-5
4-methylstyrene	* 2.58E-3		ND		< 2.58E-3	n/a	ND
2,3-benzofuran	3.59E-3		1.43E-3		2.51E-3	61	5.49E-5
1,3-dichlorobenzene	1.89E-3		2.01E-3		1.95E-3	4	7.28E-5
Pentadecane	1.86E-3		ND		< 1.86E-3	n/a	ND
C-dimethylindane	1.86E-3		1.74E-3		1.80E-3	5	9.18E-5
2-heptanone	1.61E-3		ND		< 1.61E-3	n/a	ND
p-ethyltoluene	ND		1.51E-3		< 1.51E-3	n/a	1.19E-4
Tetradecane	1.48E-3		1.43E-3		1.46E-3	2	5.09E-5
Propylbenzene	1.42E-3		ND		< 1.42E-3	n/a	5.89E-5
1,3,5-trimethylbenzene	ND		1.32E-3		< 1.32E-3	n/a	6.09E-5
Indene	** 1.04E-3		ND		< 1.04E-3	n/a	ND
o-ethyltoluene	9.77E-4		ND		< 9.77E-4	n/a	8.08E-5
2-methylnaphthalene	9.45E-4		ND		< 9.45E-4	n/a	4.49E-5
Cyclohexanone	ND		ND		ND	n/a	2.64E-4
1-decene	ND		ND		ND	n/a	2.03E-4
1-methylindan	ND		ND		ND	n/a	6.78E-5
5-ethyl-m-xylene	ND		ND		ND	n/a	5.29E-5
3-methyloctane	ND		ND		ND	n/a	5.09E-5
Tridecane	ND		ND		ND	n/a	4.59E-5
4-ethyl-o-xylene	ND		ND		ND	n/a	3.59E-5
Indan	ND		ND		ND	n/a	3.29E-5
Propylcyclohexane	ND		ND		ND	n/a	3.19E-5

* More than 50% of the compound was collected in the backup sample tube, indicating possible breakthrough

** The compound was detected in the backup sample tube but not detected in the first sample tube, indicating possible breakthrough

n/a- not applicable. Less than two runs within detectable limits.

RSD - relative standard deviation

ND - not detected

confidence lower bound of the average stack concentration. Please refer to Section 6 for further discussion of blanks and ambient samples.

Canisters. Stainless steel canisters were used to collect other VOCs with carbon number greater than 7 for which Tenax may not work well, VOCs that could contribute to ozone formation and/or OC measurement artifacts, and selected HAPs. Propene and n-butane were the two highest detected compounds with concentrations of 2.25 mg/dscm and 1.30 mg/dscm respectively (Table 4-14). All concentrations at detectable levels in the stack samples are at least five times larger than concentrations in the ambient sample, with most being an order of magnitude larger. Propane, isobutane, and isopentane are all present at significant levels in the sample, with average concentrations that are more than two standard deviations above their ambient concentrations, making them potential source apportionment marker species for process-gas firing (please refer to further discussion in Sections 6 and 7).

Elements

Element concentrations were determined by XRF analysis of the TMFs used in the dilution sampler. On average, S, Fe, Zn, Si, and Na are the most abundant elements in the stack gas (Table 4-15); however, Fe, Zn, Si, and Na were not detected at concentrations significantly greater than the ambient sample. Only Cd, P, and S were detected in more than sample and had field blank and ambient sample concentrations less than the 95% confidence lower bound of the average stack concentration (please refer to section 6 for further discussion of blanks and ambient samples). The S results are within a factor of 3 of the dilution sampler $\text{SO}_4^{=}$ results presented earlier, as expected based on comparative molecular weights, indicating that the S is present as $\text{SO}_4^{=}$ on the filters. Na and Mg results are considered semi-quantitative because of analytical limitations. Ag, As, Au, Ba, Co, Cr, Ga, Hg, In, La, Mn, Mo, Ni, Pd, Rb, Sb, Se, Sn, Sr, Tl, U, Y and Zr were below detectable levels for all sample runs.

Carbonyls (Aldehydes and Ketones)

Aldehydes were captured in a DNPH-impregnated silica gel cartridge. Results are presented in Table 4-16. All results have been field blank corrected. Formaldehyde, acetaldehyde and glyoxal had field blank and ambient sample concentrations less than the 95% confidence lower

Table 4-14. Volatile Organic Compound (VOC) Results – Canisters (Site Alpha).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Propene	3.20E-1	3.61E+0	2.82E+0	2.26E+0	2.25E+0	62	5.18E-3
n-butane	6.63E-1	2.58E+0	1.13E+0	8.31E-1	1.30E+0	67	3.30E-3
Propane	3.98E-1	1.32E+0	1.40E+0	8.54E-1	9.93E-1	47	5.52E-3
Isobutane	1.86E-1	6.44E-1	9.26E-1	8.42E-1	6.49E-1	51	3.07E-3
Cyclohexane	6.37E-2	1.04E+0	4.84E-1	1.41E-1	4.33E-1	103	2.36E-4
Ethane	4.51E-1	6.01E-1	3.36E-1	2.26E-1	4.03E-1	40	3.08E-3
1-decene	2.81E-1	2.05E-1	3.50E-1	2.46E-1	2.70E-1	23	3.22E-3
Ethene	5.16E-1	1.49E-1	2.01E-1	7.07E-2	2.34E-1	83	8.15E-4
n-hexane	4.40E-2	5.64E-1	9.98E-2	2.12E-2	1.82E-1	141	7.62E-4
Isopentane	5.70E-2	3.11E-1	2.00E-1	1.06E-1	1.69E-1	66	2.78E-3
2,3,5-trimethylhexane	7.05E-2	9.77E-2	3.30E-1	1.45E-1	1.61E-1	73	2.99E-3
Acetylene	8.93E-2	1.76E-1	1.05E-1	5.75E-2	1.07E-1	47	1.00E-3
Toluene	8.21E-2	8.31E-2	1.00E-1	6.85E-2	8.35E-2	15	2.62E-3
Methanol	1.41E-2	4.45E-3	1.16E-1	1.98E-1	8.31E-2	110	5.80E-4
Iso-butene	1.94E-2	7.01E-2	1.26E-1	9.90E-2	7.85E-2	58	7.09E-4
1-butene	1.90E-2	6.84E-2	1.22E-1	9.60E-2	7.65E-2	58	5.73E-4
Methylcyclopentane	1.53E-2	1.53E-1	5.33E-2	1.90E-2	6.01E-2	107	6.50E-4
c-2-butene	2.36E-2	6.71E-2	7.24E-2	5.64E-2	5.49E-2	40	1.95E-4
t-2-butene	1.04E-2	5.35E-2	8.28E-2	6.77E-2	5.36E-2	58	3.78E-4
Acetone	8.23E-3	4.78E-3	7.06E-2	9.14E-2	4.37E-2	100	6.69E-4
n-pentane	1.75E-2	7.55E-2	4.70E-2	2.50E-2	4.13E-2	63	1.20E-3
Benzene	1.01E-2	1.81E-2	2.63E-2	3.26E-2	2.18E-2	45	6.80E-4
Nonanal	4.55E-3	6.33E-3	3.19E-2	3.86E-2	2.03E-2	86	1.93E-3
2-methylpentane	9.38E-3	3.48E-2	2.02E-2	1.18E-2	1.90E-2	60	9.37E-4
1-pentene	2.13E-3	2.62E-2	2.82E-2	1.79E-2	1.86E-2	64	5.55E-4
m- & p-xylene	1.07E-2	1.97E-2	2.21E-2	1.59E-2	1.71E-2	29	1.26E-3
3-methylpentane	5.67E-3	3.66E-2	1.66E-2	7.63E-3	1.66E-2	85	5.99E-4
Octanal	7.29E-4	1.48E-2	2.22E-2	2.31E-2	1.52E-2	68	9.77E-4
Hexanal	1.09E-2	9.53E-3	2.22E-2	1.47E-2	1.43E-2	40	4.92E-4
Styrene + heptanal	8.10E-3	9.64E-3	1.43E-2	1.40E-2	1.15E-2	27	4.77E-4
Cyclopentane	4.05E-3	1.60E-2	1.39E-2	8.52E-3	1.06E-2	51	1.77E-4
1,3-diethylbenzene	8.56E-3	1.31E-2	1.22E-2	1.83E-3	8.92E-3	57	1.02E-4
1-hexene	2.13E-4	1.41E-2	1.97E-2	8.52E-4	8.71E-3	112	2.30E-4
t-2-pentene	2.13E-3	1.23E-2	1.06E-2	6.39E-3	7.87E-3	58	1.42E-4
2,2,5-trimethylhexane	ND	7.70E-3	ND	ND	< 7.70E-3	n/a	ND
n-decane	9.72E-3	7.91E-3	8.35E-3	4.54E-3	7.63E-3	29	2.10E-4
3-methylhexane + pentan	3.26E-3	9.94E-3	1.02E-2	6.52E-3	7.47E-3	44	4.52E-4
n-undecane	1.06E-2	7.24E-3	7.46E-3	4.31E-3	7.40E-3	35	2.69E-4
o-xylene	5.04E-3	7.99E-3	9.22E-3	7.05E-3	7.33E-3	24	4.75E-4
2,2,4-trimethylpentane	4.55E-3	1.12E-2	8.60E-3	4.34E-3	7.18E-3	47	6.79E-4
C10 olefin 2	5.96E-3	9.31E-3	8.02E-3	4.90E-3	7.05E-3	28	1.18E-5
2-methyl-1-butene	2.13E-3	1.23E-2	8.88E-3	4.69E-3	7.01E-3	64	6.44E-4
2-methyl-2-butene	3.62E-3	1.62E-2	2.17E-3	5.32E-3	6.84E-3	94	1.65E-4
n-heptane	4.13E-3	8.62E-3	8.62E-3	5.43E-3	6.70E-3	34	3.56E-4
Methylcyclohexane	3.41E-3	9.31E-3	6.28E-3	6.81E-3	6.45E-3	38	3.31E-4
2,3-dimethylbutane	2.83E-3	1.17E-2	6.65E-3	4.36E-3	6.40E-3	61	3.39E-4
C10 paraffin C	6.05E-3	8.13E-3	8.13E-3	1.08E-3	5.85E-3	57	3.60E-5
1,2,4-trimethylbenzene	4.26E-3	6.18E-3	7.84E-3	4.87E-3	5.79E-3	27	2.98E-4
C10 paraffin A	4.75E-3	7.47E-3	9.01E-3	1.08E-3	5.58E-3	62	7.79E-5
2-methylhexane	2.56E-3	8.23E-3	6.72E-3	3.83E-3	5.33E-3	49	3.54E-4

Table 4-14. Volatile Organic Compound (VOC) Results – Canisters (Site Alpha) (Continued).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
m-ethyltoluene	3.45E-3	6.60E-3	6.19E-3	4.26E-3	5.12E-3	30	3.26E-4
Isobutylbenzene	6.32E-3	4.97E-3	3.94E-3	4.69E-3	4.98E-3	20	5.09E-5
n-dodecane	8.62E-3	3.51E-3	4.17E-3	2.59E-3	4.72E-3	57	1.08E-4
MTBE	ND	8.16E-3	2.72E-3	2.68E-3	< 4.52E-3	70	1.11E-4
3,6-dimethyloctane	3.02E-3	3.29E-3	6.59E-3	4.75E-3	4.42E-3	37	9.59E-5
Ethylbenzene	3.22E-3	4.91E-3	5.74E-3	3.63E-3	4.38E-3	27	2.96E-4
3-methyl-1-butene	8.52E-4	6.71E-3	6.28E-3	3.62E-3	4.37E-3	62	4.13E-5
c-2-pentene	1.28E-3	6.93E-3	5.42E-3	3.41E-3	4.26E-3	58	7.68E-5
2,3-dimethylpentane	2.61E-3	6.85E-3	4.42E-3	2.39E-3	4.07E-3	51	4.46E-4
n-octane	3.47E-3	3.75E-3	3.97E-3	3.25E-3	3.61E-3	9	1.62E-4
2,2-dimethylbutane	1.31E-3	6.43E-3	4.44E-3	2.18E-3	3.59E-3	64	1.63E-4
2,6-dimethyloctane	2.81E-3	2.86E-3	2.64E-3	6.05E-3	3.59E-3	46	7.19E-5
2,4-dimethylpentane	1.74E-3	5.52E-3	3.98E-3	2.61E-3	3.46E-3	48	2.29E-4
1,3-dimethylcyclopentane	1.92E-3	5.85E-3	3.47E-3	2.34E-3	3.39E-3	52	1.48E-4
1,4-diethylbenzene	3.26E-3	2.90E-3	4.15E-3	2.85E-3	3.29E-3	18	2.04E-4
1,2,3,5-tetramethylbenzene	1.83E-3	2.90E-3	4.77E-3	3.46E-3	3.24E-3	38	3.96E-5
3-ethylpentane	8.67E-4	5.51E-3	3.97E-3	1.95E-3	3.07E-3	67	1.68E-4
2,3-trimethylpentane	1.52E-3	3.97E-3	2.65E-3	2.82E-3	2.74E-3	37	2.77E-4
n-nonane	2.16E-3	2.86E-3	3.52E-3	1.51E-3	2.51E-3	34	1.62E-4
p-ethyltoluene	1.42E-3	2.68E-3	3.71E-3	2.23E-3	2.51E-3	38	1.57E-4
n-propylbenzene	2.03E-3	2.68E-3	3.30E-3	2.03E-3	2.51E-3	24	1.18E-4
1,2-diethylbenzene	3.46E-3	3.94E-3	1.04E-3	1.22E-3	2.41E-3	62	1.07E-4
Cyclopentene	1.45E-3	3.99E-3	2.73E-3	1.45E-3	2.41E-3	51	1.72E-5
2-methylheptane	1.51E-3	3.74E-3	2.42E-3	1.95E-3	2.41E-3	40	1.74E-4
Heptene-1	1.28E-3	3.46E-3	ND	ND	< 2.37E-3	65	ND
1,3,5-trimethylbenzene	1.22E-3	2.89E-3	3.09E-3	2.23E-3	2.36E-3	36	1.80E-4
2,4,4-trimethyl-1-pentene	1.92E-3	2.16E-3	4.33E-3	8.52E-4	2.32E-3	63	4.13E-5
beta-pinene	3.72E-3	1.26E-3	2.10E-3	2.07E-3	2.29E-3	45	5.74E-5
Naphthalene	2.33E-3	2.57E-3	1.58E-3	2.53E-3	2.25E-3	20	5.94E-5
Ethanol + ACN	ND	2.13E-3	ND	ND	< 2.13E-3	n/a	ND
o-ethyltoluene	1.42E-3	2.89E-3	3.09E-3	8.11E-4	2.05E-3	54	9.00E-5
1,3-butadiene	4.11E-4	1.67E-3	3.13E-3	2.87E-3	2.02E-3	62	1.31E-4
C8 olefin 3	2.98E-3	2.81E-3	1.30E-3	6.39E-4	1.93E-3	59	1.18E-5
3-methylheptane	1.08E-3	2.42E-3	2.43E-3	1.52E-3	1.86E-3	36	1.44E-4
1,2,3,4-trimethylbenzene	1.83E-3	1.66E-3	1.04E-3	2.65E-3	1.79E-3	37	7.35E-5
1,2,4,5-tetramethylbenzene	1.43E-3	1.66E-3	2.70E-3	8.15E-4	1.65E-3	47	2.83E-5
1,2,3-trimethylbenzene	8.11E-4	4.53E-3	8.25E-4	4.05E-4	1.64E-3	118	2.81E-5
t-2-hexene	6.39E-4	2.60E-3	1.73E-3	1.28E-3	1.56E-3	53	4.13E-5
C10 aromatic 5	1.22E-3	1.86E-3	2.07E-3	1.02E-3	1.54E-3	33	3.96E-5
2,5-dimethylhexane	1.08E-3	1.54E-3	2.43E-3	8.67E-4	1.48E-3	47	7.82E-5
C8 paraffin 2	8.67E-4	1.76E-3	1.76E-3	1.52E-3	1.48E-3	29	6.61E-5
3-methyloctane	1.73E-3	8.80E-4	1.54E-3	1.30E-3	1.36E-3	27	1.80E-5
c-3-hexene	1.49E-3	1.30E-3	1.30E-3	1.28E-3	1.34E-3	7	1.18E-5
2-methyl-2-pentene	4.26E-4	1.95E-3	1.30E-3	1.28E-3	1.24E-3	50	4.13E-5
t-3-hexene + chloroform	ND	2.16E-3	1.08E-3	4.26E-4	< 1.22E-3	72	1.77E-5
2,5-dimethylheptane	8.65E-4	1.76E-3	1.54E-3	6.49E-4	1.20E-3	44	6.00E-5
C9 olefin 3	4.26E-4	8.66E-4	2.60E-3	8.52E-4	1.19E-3	81	5.32E-5
Octene-1	1.28E-3	1.08E-3	1.08E-3	1.28E-3	1.18E-3	10	5.32E-5
Isopropyltoluene	6.11E-4	1.24E-3	1.45E-3	1.22E-3	1.13E-3	32	1.70E-5
1,1-dimethylcyclohexane	4.26E-4	1.08E-3	4.33E-4	2.56E-3	1.12E-3	89	4.73E-5

Table 4-14. Volatile Organic Compound (VOC) Results – Canisters (Site Alpha) (Continued).

Parameter	Value						
Units	mg/dscm					(%)	mg/dscm
Run Number	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Indan	1.20E-3	1.22E-3	1.01E-3	9.97E-4	1.11E-3	11	7.19E-5
C10 aromatic 2	1.43E-3	1.04E-3	8.29E-4	1.02E-3	1.08E-3	23	6.22E-5
1-methylcyclopentene	2.08E-4	1.90E-3	1.48E-3	6.24E-4	1.05E-3	74	2.31E-5
C10 aromatic 6	1.02E-3	2.07E-3	6.22E-4	4.08E-4	1.03E-3	72	1.13E-5
1-methylindan	1.40E-3	1.02E-3	6.13E-4	ND	< 1.01E-3	39	1.11E-5
c-2-hexene	ND	1.52E-3	1.30E-3	2.13E-4	< 1.01E-3	69	ND
Isopropylcyclohexane	6.39E-4	1.30E-3	1.30E-3	6.39E-4	9.69E-4	39	5.91E-5
trans-3-methyl-2-pentene	4.26E-4	1.73E-3	8.67E-4	8.52E-4	9.69E-4	57	4.13E-5
Indene	7.84E-4	7.97E-4	9.97E-4	7.84E-4	8.40E-4	12	2.72E-5
C11 aromatic 1	4.09E-4	1.04E-3	1.04E-3	ND	< 8.30E-4	44	1.70E-5
3,3-dimethylpentane	6.52E-4	8.84E-4	1.33E-3	4.35E-4	8.24E-4	46	3.62E-5
C9 paraffin 1	4.33E-4	1.10E-3	1.10E-3	6.49E-4	8.21E-4	41	3.00E-5
2,6-dimethylheptane	8.65E-4	1.10E-3	6.60E-4	6.49E-4	8.19E-4	26	3.60E-5
2,3-dimethylhexane	1.73E-3	4.41E-4	6.62E-4	4.34E-4	8.18E-4	76	1.20E-5
2-methyl-1-pentene	2.13E-4	1.52E-3	8.67E-4	6.39E-4	8.08E-4	67	2.36E-5
t-3-heptene	ND	8.66E-4	1.08E-3	4.26E-4	< 7.92E-4	42	2.95E-5
C10 aromatic 1	6.11E-4	1.04E-3	8.29E-4	6.11E-4	7.72E-4	26	2.26E-5
4-methylheptane	2.16E-4	1.32E-3	4.40E-4	1.08E-3	7.65E-4	68	6.60E-5
4,4-dimethylheptane	6.49E-4	8.80E-4	6.60E-4	8.65E-4	7.64E-4	17	5.40E-5
C9 olefin 1	6.39E-4	6.49E-4	1.30E-3	4.26E-4	7.54E-4	50	2.36E-5
C8 olefin 1	4.26E-4	8.66E-4	1.08E-3	6.39E-4	7.53E-4	38	3.54E-5
cis-3-methyl-2-pentene	4.26E-4	1.08E-3	8.67E-4	6.39E-4	7.53E-4	38	2.36E-5
C6 olefin	6.39E-4	8.66E-4	6.50E-4	8.52E-4	7.52E-4	17	1.18E-5
C9 olefin 4	6.39E-4	4.33E-4	8.67E-4	8.52E-4	6.98E-4	29	ND
Limonene	1.03E-3	4.21E-4	6.31E-4	6.20E-4	6.77E-4	38	5.16E-5
C11 paraffin A	6.47E-4	6.58E-4	ND	ND	< 6.53E-4	1	2.39E-5
C7 olefin 1	ND	1.08E-3	4.33E-4	4.26E-4	< 6.47E-4	58	1.77E-5
Isopropylbenzene	4.05E-4	6.18E-4	1.03E-3	2.03E-4	5.64E-4	63	4.50E-5
3,3-dimethylheptane	2.16E-4	1.10E-3	4.40E-4	4.33E-4	5.47E-4	70	3.00E-5
C8 paraffin 3	ND	4.41E-4	4.41E-4	4.34E-4	< 4.38E-4	1	1.20E-5
C9 paraffin 3	4.33E-4	4.40E-4	6.60E-4	2.16E-4	4.37E-4	41	2.40E-5
Dodecene-1	4.31E-4	2.19E-4	ND	6.47E-4	< 4.32E-4	49	ND
4-methylhexene	2.13E-4	4.33E-4	8.67E-4	2.13E-4	4.31E-4	71	1.77E-5
Nonene-1	ND	6.49E-4	2.17E-4	4.26E-4	< 4.31E-4	50	1.77E-5
C7 olefin 2	4.26E-4	4.33E-4	ND	ND	< 4.29E-4	1	5.91E-6
Cyclohexene	2.08E-4	8.45E-4	4.23E-4	2.08E-4	4.21E-4	71	2.31E-5
C10 aromatic 4	4.08E-4	4.14E-4	6.22E-4	2.04E-4	4.12E-4	41	2.26E-5
Benzaldehyde	ND	4.68E-4	4.68E-4	2.30E-4	< 3.89E-4	35	5.11E-5
Chlorobenzene	2.85E-4	2.90E-4	2.90E-4	5.70E-4	3.58E-4	39	1.58E-5
sec-butylbenzene	4.08E-4	2.07E-4	ND	ND	< 3.07E-4	46	5.65E-6
C9 paraffin 2	4.33E-4	2.20E-4	2.20E-4	2.16E-4	2.72E-4	39	1.80E-5
2,4-dimethylhexane	2.17E-4	2.20E-4	2.21E-4	2.17E-4	2.19E-4	1	1.80E-5
C8 olefin 2	2.13E-4	ND	2.17E-4	ND	< 2.15E-4	1	5.91E-6
Isoprene	ND	ND	ND	ND	ND	n/a	2.29E-5
2-methylpropanal	ND	ND	ND	ND	ND	n/a	2.28E-5
C11 aromatic 3	ND	ND	ND	ND	ND	n/a	1.70E-5
2,4-dimethylheptane	ND	ND	ND	ND	ND	n/a	1.20E-5
Total Identified NMHC	3.50E+0	1.21E+1	9.33E+0	6.49E+0	7.86E+0	47	5.37E-2
Unidentified	2.77E-1	3.41E-1	4.48E-1	4.32E-1	3.74E-1	21	7.05E-3

ND - Not Detected

n/a- not applicable. Less than two runs within detectable limits.

Table 4-15. Elements, as Measured by the Dilution Sampler (Site Alpha).

Parameter	Value							
Units	mg/dscm					%	mg/dscm	
Run Date	Run 1 15-Feb-01	Run 2 16-Feb-01	Run 3 20-Feb-01	Run 4 21-Feb-01	Average	RSD	Ambient 22-Feb-01	MDL (2)
Al	1.55E-03	3.16E-04	3.51E-04	4.14E-04	6.58E-04	91	4.62E-4	1.74E-4
Br	ND	ND	1.92E-05	2.65E-05	< 2.29E-05	23	4.25E-6	1.74E-5
Ca	9.12E-04	2.94E-04	2.17E-04	3.09E-04	4.33E-04	74	4.77E-4	7.82E-5
Cd	2.76E-04	4.20E-04	ND	ND	< 3.48E-04	29	ND	2.08E-4
Cl	1.88E-04	ND	1.06E-03	2.48E-04	< 4.98E-04	98	1.71E-3	1.74E-4
Cr	ND	ND	ND	ND	ND	n/a	1.57E-6	3.30E-5
Cu	8.10E-04	1.20E-04	1.42E-04	1.17E-03	5.60E-04	92	1.58E-5	1.91E-5
Fe	1.12E-02	2.29E-04	2.13E-04	3.15E-04	2.98E-03	183	8.42E-4	2.61E-5
K	1.11E-04	ND	1.41E-04	ND	< 1.26E-04	17	2.69E-4	1.06E-4
Mg	6.19E-04	4.32E-04	9.47E-05	4.89E-04	4.09E-04	55	1.31E-4	(1)
Mn	ND	ND	ND	ND	ND	n/a	1.39E-5	2.78E-5
Na	1.93E-04	4.76E-04	1.78E-03	7.84E-04	8.07E-04	85	6.01E-4	(1)
Ni	ND	ND	ND	ND	ND	n/a	1.35E-6	1.55E-5
P	1.05E-04	ND	1.45E-04	ND	< 1.25E-04	22	ND	9.73E-5
Pb	ND	ND	ND	8.58E-05	< 8.58E-05	n/a	1.23E-5	5.21E-5
Rb	ND	ND	ND	ND	ND	n/a	1.15E-6	1.74E-5
S	7.36E-03	1.26E-02	4.99E-03	1.95E-02	1.11E-02	58	4.44E-4	8.69E-5
Si	1.10E-03	6.61E-04	4.73E-04	8.74E-04	7.78E-04	35	1.45E-3	1.09E-4
Sr	ND	ND	ND	ND	ND	n/a	4.93E-6	1.91E-5
Ti	ND	ND	ND	6.20E-05	< 6.20E-05	n/a	7.64E-5	5.04E-5
Tl	ND	ND	ND	ND	ND	n/a	1.27E-6	4.34E-5
V	ND	ND	5.54E-05	ND	< 5.54E-05	n/a	6.84E-6	4.34E-5
Zn	6.25E-03	ND	1.11E-04	4.20E-04	< 2.26E-03	153	3.79E-5	1.91E-5
Zr	ND	ND	ND	ND	ND	n/a	1.05E-6	2.95E-5

(1) No detection limits given. Zeroes treated as non-detect. Data is semi-quantitative.

(2) Average method detection limit for dilution ratio. Ambient sample MDLs are smaller due to 1:1 dilution ratio.

MDL- Method Detection Limit

ND- Not detected

n/a- not applicable; only one run within detectable limits.

RSD- Relative standard deviation

Table 4-16. Carbonyl Results (mg/dscm) (Site Alpha).

Run		Run 1	Run 2	Run 3	Run 4	Average	RSD (%)	Ambient
Date	Units	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01			22-Feb-01
Formaldehyde	mg/dscm	8.18E-2	6.45E-2	5.10E-2	8.92E-2	7.16E-2	24	1.52E-3
	ppb	65.6	51.7	40.9	71.5	57.4	24	1.22
Acetaldehyde	mg/dscm	4.46E-2	5.80E-2	6.99E-2	1.33E-1	7.63E-2	51	1.81E-3
Glyoxal	mg/dscm	1.98E-2	1.44E-2	1.84E-2	1.82E-2	1.77E-2	13	5.99E-4

ND - not detected

n/a- not applicable; only one run within detectable limits.

RSD - relative standard deviation

bound of the average stack concentration (please refer to section 6 for further discussion of blanks and ambient samples). Acetone was also present, but the data is not reliable due to the use of acetone in the same recovery area where the cartridges were stored and the use of acetone to clean the dilution sampler. A backup cartridge was in place during Run 4 to check for breakthrough.

The concentrations detected in the backup are approximately half those in the front sample, indicating that there may be significant breakthrough. Additional backup samples will be taken in future tests to determine if breakthrough is a consistent problem.

Secondary Particle Precursors

Gaseous ammonia was captured on a citric acid-impregnated cellulose-fiber filter downstream of the quartz filter used for ions and OC/EC analysis. SO₂ was captured on a potassium carbonate impregnated cellulose-fiber filter downstream of a quartz filter. Results are presented in Table 4-17. Both SO₂ and ammonia had field blank and ambient sample concentrations less than the 95% confidence lower bound of the average stack concentration (please refer to section 6 for further discussion of blanks and ambient samples). The SO₂ captured by the filter accounts for approximately 67 percent of the total reduced sulfur contained in the fuel. The NO_x results presented in the table were obtained from the facility CEMS system.

Table 4-17. Secondary PM Precursor Results (Site Alpha).

Parameter	Units	Value						
Run Number	-	Run 1	Run 2	Run 3	Run 4	Average	RSD	Ambient
Date	-	15-Feb-01	16-Feb-01	20-Feb-01	21-Feb-01		(%)	22-Feb-01
Ammonia	mg/dscm	0.181	0.188	0.255	0.165	0.197	20	1.07E-3
	ppm	0.256	0.266	0.361	0.233	0.279	20	1.52E-3
	lb/hr	0.0393	0.0401	0.0542	0.0320	0.0414	22	n/a
Sulfur Dioxide	mg/dscm	20.4	30.6	26.5	31.1	27.1	18	8.67E-4
	ppm	7.67	11.5	9.94	11.7	10.2	18	3.26E-4
	lb/hr	4.43	6.50	5.61	6.05	5.65	16	n/a
NO _x	mg/dscm	147	178	163	158	161	8	n/a
	ppm	76.6	93.0	85.23	82.5	84.4	8	n/a
	lb/hr	31.8	37.9	34.6	30.7	33.7	9	n/a

n/a - not applicable

ND - not detected

RSD- Relative standard deviation

Section 5

EMISSION FACTORS AND SPECIATION PROFILES

Emission factors were determined by dividing the emission rate, in lb/hr, by the measured heat input, in MMBtu/hr, to give pounds per million British thermal units (lb/MMBtu). Heat input is the product of the measured fuel flow rate and the average fuel heating value (based on fuel grab sample analysis). Average emission factors were determined by averaging detected data.

Undetected data, data with only one detected run, data with uncertainty greater than 100 percent and data with average concentrations less than field blank concentrations are excluded from tables.

UNCERTAINTY

An uncertainty analysis was performed to determine the 95 percent confidence interval and to estimate the upper limit of the measured emission factor and the mass speciation results (ASME, 1990). In the tables that follow, the reported results, the total uncertainty, a 95 percent confidence upper bound, and the number of detected runs are given for each of the substances of interest. The total uncertainty represents the 95 percent confidence interval based on a two-tailed Student “t” distribution. The 95 percent confidence upper bound estimate is based on the single-tailed Student “t” distribution at the 95 percent confidence level.

EMISSION FACTORS

Table 5-1 presents emission factors for primary emissions, including filterable and condensable particulate mass, and elements and ions as measured on the dilution sampler filters. FPM includes all particulate captured in the in-stack cyclones, probe and filter. Total CPM is blank corrected in accordance with Method 202 guidelines. Emission factors with an uncertainty greater than 100 percent have been excluded from tables because these data are considered unrepresentative.

The average emission factor for total PM_{2.5} (including CPM) measured using in-stack/impinger train methods is more than two orders of magnitude higher than the emission factor for PM_{2.5} by the dilution sampler; the total PM_{2.5} emission factor for the in-stack methods with the unpurged

train is 157 times higher than the dilution sampler emission factor. As noted previously, this difference is believed to be due to sampling and analytical artifacts associated with the CPM measurement method (i.e., conversion of SO₂ to CPM in the impinger train and over saturation of vapor phase species compared to the stack plume, discussed further in Section 7). As a result of this artifact, the emission factor derived from the dilution sampler results is considered more representative of the true source emissions. Further investigations are planned at a pilot scale facility and in field tests to investigate this artifact further.

Table 5-1. Primary Emissions- Particulate Mass and Elements (Site Alpha).

Substance		Emission Factor (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
Particulate Mass	PM _{2.5} mass (Dilution Sampler)	< 5.23E-5	43	6.91E-5	3
Elements	S	1.39E-5	94	2.36E-5	4
	Si	9.98E-7	79	1.69E-6	4
Ions	NO ₃ ⁻	8.68E-6	77	1.37E-5	4
	SO ₄ ⁼	3.59E-5	92	6.06E-5	4
	Soluble Na	3.43E-7	43	4.70E-7	4
Particulate Mass (Manual methods)	Organic CPM (unpurged train)	1.06E-3 *	76	1.67E-3	4
	Inorganic CPM (unpurged train)	6.62E-3 *	98	1.14E-2	4
	Total CPM (unpurged train)	7.77E-3 *	93	1.32E-2	4
	Organic CPM (purged train)	1.61E-3 *	43	2.16E-3	4
	Inorganic CPM (purged train)	2.22E-2 *	57	3.18E-2	4
	Total CPM (purged train)	2.41E-2 *	53	3.39E-2	4
	Total Filterable PM (Method 17, unpurged train)	5.49E-4 *	36	7.06E-4	4
	Total Filterable PM (Method PRE-4, purged train)	8.89E-4 *	89	1.49E-3	4
	Filterable PM ₁₀ (Method PRE-4, purged train)	5.89E-4 *	75	9.23E-4	4
	Filterable PM _{2.5} (Method PRE-4, purged train)	4.36E-4 *	76	6.85E-4	4

* Emission factors not recommended for emission estimation purposes.

Table 5-2 presents emission factors for OC and total carbon, and SVOCs as measured by the dilution sampler. SVOC emission factors are low and compounds whose uncertainty is greater than 100 percent are not included in the tables. In addition, compounds whose average emission factor is less than the level in the field blank are excluded as well. The average sum of all SVOCs equals 5.5x10⁻⁶ lb/MMBtu. The carbon mass associated with the SVOCs accounts for approximately 4.9 percent of the total organic carbon. However, the quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs in the sample. A backup quartz filter was sampled behind the TMF to measure the magnitude of this absorptive

bias, and showed a concentration of OC on the same order as that in the sample. Additional discussion of this bias is located in Section 7. 1,3+1,6+1,7-dimethylnaphthalene, 2-ethyl-1-methylnaphthalene, and acenaphthylene are present at levels significantly above (greater than two standard deviations) their ambient concentrations. Since the dilution samples are expected to collect SVOCs that condense in the plume, these results are especially useful for receptor modeling purposes.

Table 5-2. Primary Emissions- Carbon and SVOCs (Site Alpha).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
Organic Carbon	9.26E-5 *	21	1.11E-4	4
Total Carbon	1.03E-4	25	1.26E-4	4
Semi-Volatile Organic Compounds				
1+2-ethylnaphthalene	5.37E-7	72	8.31E-7	4
2,6+2,7-dimethylnaphthalene	8.57E-7	85	1.41E-6	4
1,3+1,6+1,7-dimethylnaphthalene	1.43E-6	84	2.33E-6	4
A-trimethylnaphthalene	2.70E-7	80	4.34E-7	4
1-ethyl-2-methylnaphthalene	1.00E-7	52	1.43E-7	4
B-trimethylnaphthalene	2.11E-7	68	3.21E-7	4
C-trimethylnaphthalene	2.31E-7	54	3.28E-7	4
2-ethyl-1-methylnaphthalene	< 1.02E-6	97	1.71E-6	3
E-trimethylnaphthalene	9.61E-8	66	1.47E-7	4
2,3,5+I-trimethylnaphthalene	1.47E-7	79	2.37E-7	4
J-trimethylnaphthalene	9.85E-8	56	1.42E-7	4
Phenanthrene	1.43E-7	91	2.43E-7	4
2-methylphenanthrene	2.96E-8	83	5.11E-8	4
Acenaphthylene	< 3.31E-7	76	5.24E-7	2
OC Backup Filter**	9.74E-5	37	1.30E-4	4

* OC is subject to potential positive bias from adsorption of VOC on the filter. Refer to Sections 6 & 7 for further discussion.

** OC measured on a backup" quartz fiber filter placed downstream of Teflon membrane filter - not included in sum of species calculations. Refer to Sections 6 & 7 for further discussion.

Emission factors for VOCs obtained from the Tenax samples with carbon number greater than seven (i.e., secondary fine PM precursors) are presented in Table 5-3. Benzaldehyde, benzoic acid, hexadecanoic acid, phenol, and acetophenone are potential Tenax degradation products, causing their emission factors to have a high degree of uncertainty. The emission factors for these compounds, as well as those for compounds whose uncertainties are greater than 100 percent and for compounds whose average stack sample concentration is less than the level in the field blank are excluded from the tables because they are considered unrepresentative. The loss

of Runs 2 and 4, combined with the high uncertainty from the Tenax degradation products makes it difficult to draw significant conclusions from the Tenax data.

Table 5-3. Secondary Fine PM Precursors (VOCs) – Tenax (Site Alpha).

Substance	Average (lb/MMBtu)	Uncertainty	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
o-xylene	6.57E-6	67	8.92E-6	4
C-dimethylindane	2.42E-6	66	3.29E-6	4
m & p-xylene	1.84E-5	66	2.49E-5	4
1,3-dichlorobenzene	2.62E-6	65	3.55E-6	4
m-ethyltoluene	4.47E-6	59	5.93E-6	4
Tetradecane	1.96E-6	56	2.57E-6	4

Emission factors for VOCs with carbon number greater than two were obtained from the canister samples and are presented in Table 5-4. The emission factors for compounds whose uncertainties are greater than 100 percent and for compounds whose average stack sample concentration is less than the level in the field blank are excluded from the tables because they are considered unrepresentative. Propane, isobutane, and isopentane are all present at significant levels in the sample, with average concentrations that are more than two standard deviations above their ambient concentrations, making them potential marker species for process-gas firing (see further discussion in Section 7).

Carbonyl emission factors are presented in Table 5-5. Formaldehyde and acetaldehyde are present at approximately the same levels. The emission factor for formaldehyde (9.1×10^{-5}) is approximately 1.7 times higher than that found in the EPA FIRE 4.23 database (5.5×10^{-5}) for a process gas-fired process heater with no emission controls; however, the formaldehyde emission factor 95% confidence lower bound (5.6×10^{-5}) is approximately equal to the EPA FIRE 4.23 database value, suggesting that determining whether the Alpha and EPA FIRE 4.23 database emission factors are significantly different will require additional data.

Emission factors for secondary PM_{2.5} precursors (SO₂, NH₃, and NO_x) are presented in Table 5-6. The NO_x results presented in the table were obtained from the facility CEMS system.

Table 5-4. Secondary Fine PM Precursors (VOCs) – Canisters (Site Alpha).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
Propane	1.27E-3	79	2.04E-3	4
Isobutane	8.17E-4	85	1.35E-3	4
Ethane	5.22E-4	69	8.03E-4	4
1-decene	3.48E-4	45	4.79E-4	4
Acetylene	1.38E-4	79	2.22E-4	4
Toluene	1.07E-4	37	1.42E-4	4
Iso-butene	9.90E-5	96	1.71E-4	4
1-butene	9.64E-5	96	1.67E-4	4
c-2-butene	6.97E-5	69	1.07E-4	4
t-2-butene	6.75E-5	96	1.17E-4	4
Benzene	2.73E-5	77	4.35E-5	4
2-methylpentane	2.44E-5	100	4.28E-5	4
m- & p-xylene	2.18E-5	54	3.13E-5	4
Hexanal	1.83E-5	69	2.82E-5	4
Styrene + heptanal	1.46E-5	51	2.07E-5	4
Cyclopentane	1.35E-5	85	2.24E-5	4
1,3-diethylbenzene	1.17E-5	95	2.01E-5	4
t-2-pentene	1.00E-5	96	1.73E-5	4
n-decane	9.92E-6	53	1.42E-5	4
n-undecane	9.64E-6	61	1.43E-5	4
3-methylhexane + pentanal	9.52E-6	75	1.50E-5	4
o-xylene	9.35E-6	47	1.30E-5	4
2,2,4-trimethylpentane	9.23E-6	79	1.48E-5	4
C10 olefin 2	9.07E-6	53	1.29E-5	4
n-heptane	8.57E-6	61	1.27E-5	4
Methylcyclohexane	8.18E-6	66	1.24E-5	4
C10 paraffin C	7.65E-6	95	1.32E-5	4
1,2,4-trimethylbenzene	7.42E-6	51	1.05E-5	4
2-methylhexane	6.82E-6	82	1.11E-5	4
m-ethyltoluene	6.55E-6	54	9.42E-6	4
Isobutylbenzene	6.41E-6	42	8.68E-6	4
n-dodecane	6.20E-6	94	1.07E-5	4
3,6-dimethyloctane	5.63E-6	65	8.51E-6	4
Ethylbenzene	5.61E-6	50	7.91E-6	4
c-2-pentene	5.42E-6	96	9.36E-6	4
2,3-dimethylpentane	5.23E-6	85	8.64E-6	4
n-octane	4.63E-6	31	5.95E-6	4
2,6-dimethyloctane	4.50E-6	78	7.20E-6	4
2,4-dimethylpentane	4.42E-6	81	7.17E-6	4
1,3-dimethylcyclopentane	4.34E-6	87	7.23E-6	4
1,4-diethylbenzene	4.23E-6	40	5.68E-6	4
1,2,3,5-tetramethylbenzene	4.13E-6	66	6.26E-6	4
2,3-trimethylpentane	3.47E-6	64	5.23E-6	4
n-nonane	3.25E-6	61	4.83E-6	4
n-propylbenzene	3.22E-6	47	4.48E-6	4
p-ethyltoluene	3.21E-6	66	4.88E-6	4
Cyclopentene	3.09E-6	85	5.11E-6	4

Table 5-4. Secondary Fine PM Precursors (VOCs) – Canisters (Site Alpha) (Continued).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
2-methylheptane	3.07E-6	69	4.74E-6	4
1,3,5-trimethylbenzene	3.00E-6	63	4.50E-6	4
beta-pinene	2.97E-6	77	4.74E-6	4
Naphthalene	2.88E-6	42	3.91E-6	4
o-ethyltoluene	2.66E-6	91	4.50E-6	4
C8 olefin 3	2.53E-6	98	4.43E-6	4
3-methylheptane	2.38E-6	64	3.58E-6	4
1,2,3,4-trimethylbenzene	2.27E-6	65	3.43E-6	4
1,2,4,5-tetramethylbenzene	2.14E-6	80	3.46E-6	4
C10 aromatic 5	1.99E-6	59	2.92E-6	4
t-2-hexene	1.99E-6	88	3.33E-6	4
2,5-dimethylhexane	1.91E-6	79	3.08E-6	4
C8 paraffin 2	1.88E-6	53	2.69E-6	4
3-methyloctane	1.76E-6	51	2.49E-6	4
c-3-hexene	1.72E-6	30	2.21E-6	4
2-methyl-2-pentene	1.57E-6	85	2.58E-6	4
2,5-dimethylheptane	1.55E-6	75	2.46E-6	4
Octene-1	1.51E-6	31	1.95E-6	4
Isopropyltoluene	1.44E-6	58	2.10E-6	4
Indan	1.42E-6	32	1.84E-6	4
C10 aromatic 2	1.39E-6	46	1.92E-6	4
Isopropylcyclohexane	1.25E-6	68	1.91E-6	4
trans-3-methyl-2-pentene	1.23E-6	94	2.11E-6	4
Indene	1.08E-6	34	1.41E-6	4
3,3-dimethylpentane	1.07E-6	79	1.72E-6	4
2,6-dimethylheptane	1.05E-6	49	1.48E-6	4
C9 paraffin 1	1.05E-6	70	1.62E-6	4
C10 aromatic 1	9.90E-7	50	1.39E-6	4
C9 olefin 1	9.77E-7	84	1.61E-6	4
4,4-dimethylheptane	9.71E-7	38	1.29E-6	4
C8 olefin 1	9.64E-7	66	1.46E-6	4
cis-3-methyl-2-pentene	9.61E-7	66	1.46E-6	4
C6 olefin	9.56E-7	38	1.27E-6	4
C9 olefin 4	8.89E-7	54	1.28E-6	4
Limonene	8.77E-7	66	1.33E-6	4
C9 paraffin 3	5.69E-7	71	8.84E-7	4
C10 aromatic 4	5.36E-7	71	8.33E-7	4
Chlorobenzene	4.51E-7	68	6.91E-7	4
C9 paraffin 2	3.54E-7	68	5.43E-7	4
2,4-dimethylhexane	2.80E-7	27	3.55E-7	4
C8 paraffin 3	< 5.48E-7	29	6.99E-7	3
Benzaldehyde	< 4.93E-7	93	8.16E-7	3
C11 paraffin A	< 8.64E-7	57	1.18E-6	2
C7 olefin 2	< 5.69E-7	57	7.74E-7	2
C8 olefin 2	< 2.89E-7	57	3.93E-7	2
Total Identified NMHC	1.00E-2	80	1.62E-2	4
Unidentified	4.76E-4	44	6.50E-4	4

Table 5-5. Carbonyl (Aldehyde) Emission Factors (Site Alpha).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound	Number of Detected
Formaldehyde	9.12E-5	47	1.27E-4	4
Acetaldehyde	9.51E-5	86	1.58E-4	4
Glyoxal	2.27E-5	34	2.97E-5	4

Table 5-6. Secondary Particle Precursors (Site Alpha).

Substance	Average (lb/MMBtu)	Uncertainty (%)	95% Confidence Upper Bound (lb/MMBtu)	Number of Detected Runs
NH ₃	2.54E-4	36	3.26E-4	4
SO ₂	3.45E-2	34	4.38E-2	4
NO _x	2.06E-1	22	2.46E-1	4

PM2.5 SPECIATION PROFILES

Dilution Sampler

The speciation profile for PM2.5, based on dilution sampler results, is given in Table 5-7. This table includes all results from the ED-XRF analysis of the dilution sampler TMFs, the ion analysis of the dilution sampler quartz filters and the OC/EC analysis of the dilution sampler quartz filters that had emission factors with uncertainties less than 100 percent as presented in Table 5-1. The mass fractions presented are the ratio of the emission factor of the emitted compound over the sum of the species emission factors, assuming the highest stable oxide for the metallic species and correcting OC for C and H in SVOC. The majority of the mass is OC; however, as discussed in Section 7 and shown by the backup filter OC value in Table 5-7, the OC may be subject to a significant positive bias from filter adsorption of VOC. The mass fractions presented in Table 5-7 should only be used in conjunction with PM2.5 values generated from dilution sampling; application to PM results from traditional manual methods will result in erroneous speciation estimation.

Table 5-7. Speciation Profile for Primary Emissions – Dilution Sampler Results (Site Alpha).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
OC*	61	42	83
SO ₄ ⁼	17	99	29
NO ₃ ⁻	4.1	85	6.8
Si	1.0	87	1.7
Soluble Na	0.45	49	0.63
Backup Filter OC **	58	54	83

* OC measurements are subject to a potential positive bias from adsorption of VOC species. Refer to footnote ** and Sections 6 & 7 for further discussion.

** OC measured on a "backup" quartz fiber filter placed downstream of Teflon membrane filter included in sum of species calculations. Refer to Sections 6 & 7 for further discussion.

1- Mass fraction is emission factor of species divided by emission factor of sum of species - calculated from highest stable oxide form of elements. Speciation profile should only be applied to PM_{2.5} mass obtained from dilution sampling; any application to emission factors obtained from manual methods will result in erroneous calculations.

The average emission factor for the sum of species (1.8×10^{-4} lb/MMBtu) is approximately four times greater than the average emission factor for total PM_{2.5} mass (5.2×10^{-5} lb/MMBtu, measured gravimetrically). This difference may be due to the bias associated with the different analytical methods used to determine the speciation of the mass versus the gravimetric analysis used to measure total PM_{2.5} mass. In addition, two different types of filters were used: TMFs were used for the elemental analysis and particulate mass, while quartz filters were used for OC/EC analysis and ionic analysis. It is possible that variations in particle deposition occurred between the different filters, resulting in a bias. Inhomogeneous deposition on the filter could also cause a bias. The OC/EC analysis and ion analysis each take only part of the filter for analysis, and the total mass on the filter is normalized assuming that this mass is evenly distributed over the collection area. However, differences in particle collection efficiency among the different filter types or variations in deposition on the filters are unlikely causes. The quartz filters used for OC/EC analysis have the potential for positive OC bias due to absorption of VOCs in the sample. This bias is more pronounced in cleaner sources, such as gas-fired combustion. Additional discussion of this bias is located in Section 7.

Figure 5-1 shows the data presented in Table 5-7. The majority of the mass (55 percent) is composed of organic carbon, with sulfate being the next most abundant constituent (19 percent). Compounds with all runs below detectable levels are not included in the figure. Only those compounds presented in Table 5-7 are included in the figure. The error bars on the figure represent one standard deviation of the results.

Organic Aerosols

Table 5-8 shows the organic aerosol speciation profile, expressed as a mass fraction. This mass fraction is determined by dividing the average emission factor of the equivalent carbon mass of the emitted quantity by the average emission factor of total organic carbon, both in units of lb/MMBtu. The speciated organic carbon, measured as SVOCs, accounts for approximately 5 percent of the total organic carbon. The data from Table 5-8 are shown in Figure 5-2. The error bars on the figure represent the standard deviation of the results. A high standard deviation indicates a greater uncertainty in the results, which is due to the variation in the SVOC concentrations as well as the variability of the OC concentration.

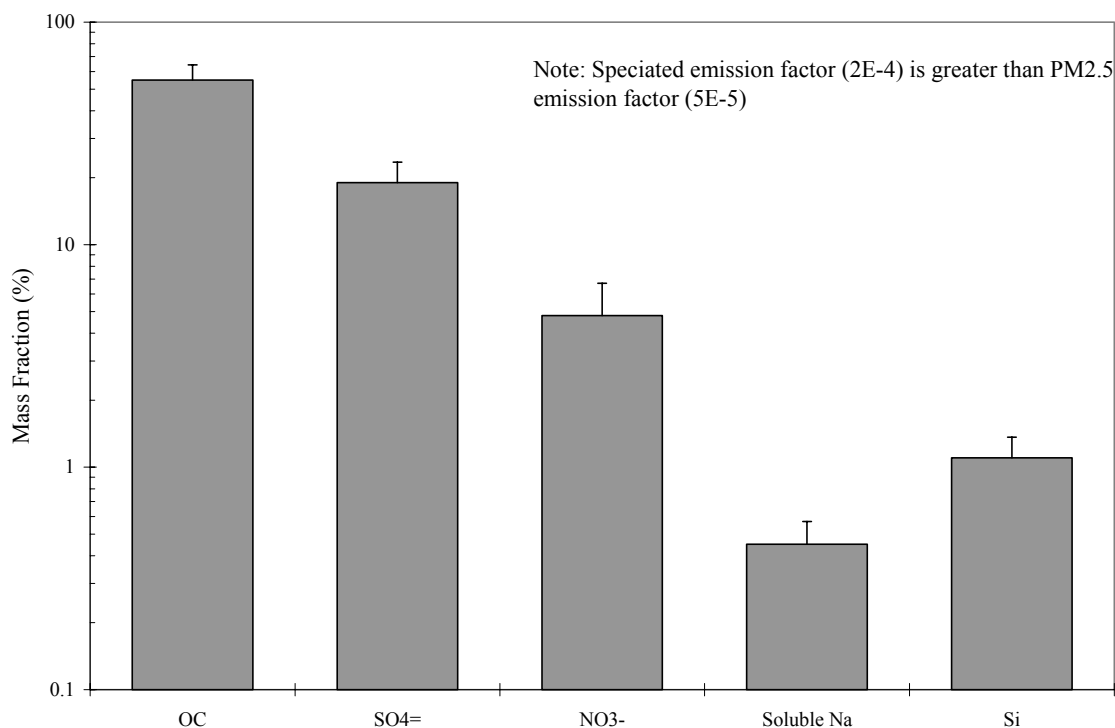


Figure 5-1. PM2.5 Speciation, as Measured by the Dilution Sampler (Site Alpha).

Table 5-8. Organic Aerosol Speciation Profile (Site Alpha).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (Mass Fraction %)
1,3+1,6+1,7-dimethylnaphthalene	1.37	86	2.28
2,6+2,7-dimethylnaphthalene	0.82	87	1.38
2-ethyl-1-methylnaphthalene	0.73	129	1.44
1+2-ethylnaphthalene	0.52	75	0.82
A-trimethylnaphthalene	0.26	83	0.42
C-trimethylnaphthalene	0.23	58	0.33
B-trimethylnaphthalene	0.20	71	0.32
Acenaphthylene	0.16	192	0.39
Phenanthrene	0.14	94	0.25
2,3,5+I-trimethylnaphthalene	0.14	82	0.23
J-trimethylnaphthalene	0.10	60	0.15
1-ethyl-2-methylnaphthalene	0.10	56	0.14
E-trimethylnaphthalene	0.09	70	0.15
2-methylphenanthrene	0.03	85	0.05

1- SVOC carbon mass expressed as a percent of total organic carbon mass.

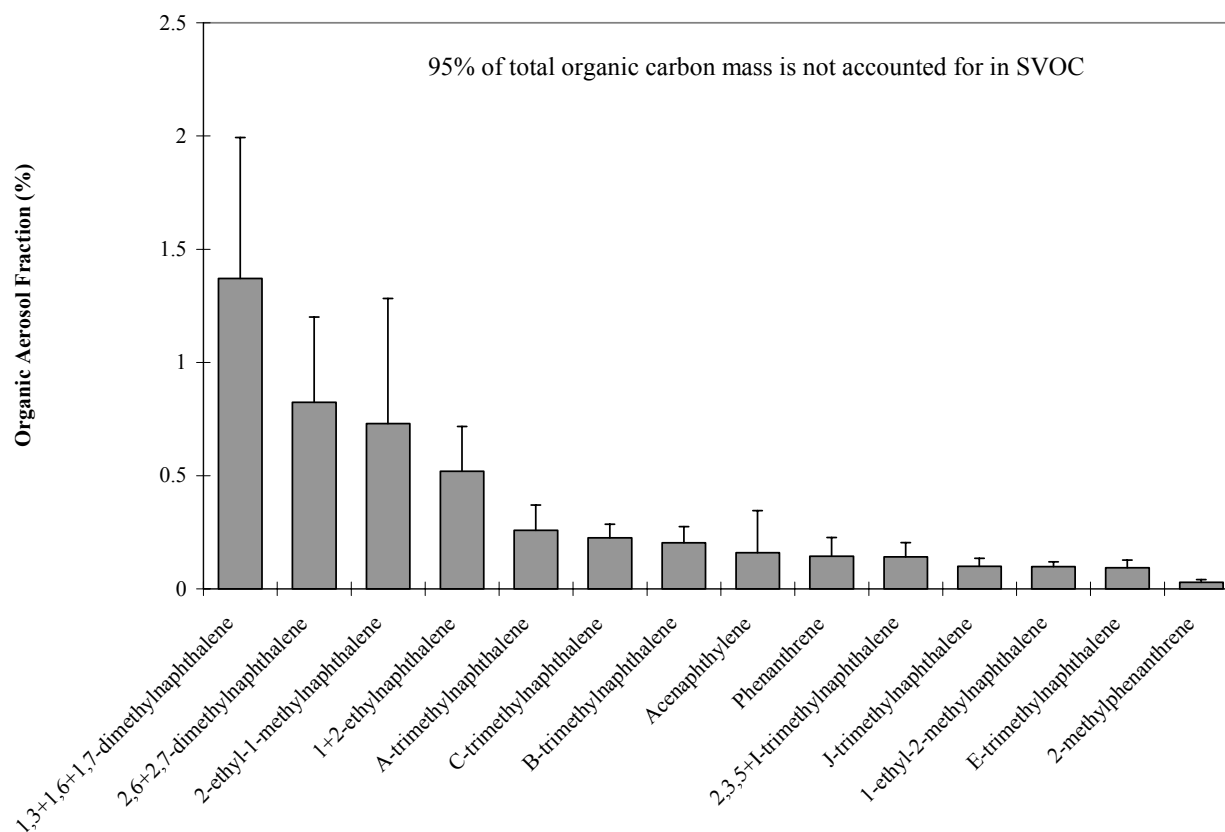


Figure 5-2. Organic Aerosol Speciation (Site Alpha).

Method PRE-4/202

As noted previously, the dilution sampler results are considered the most representative of true PM_{2.5} emissions due to artifacts associated with Method 202 that lead to positive bias in the sulfate and mass results. The speciation profile is presented here only for comparative purposes and should not be used for other purposes. Table 5-9 shows the speciation profile of the PM_{2.5} mass as measured by Method PRE-4/202 for the Standard Method results. Mass fraction is the ratio of the measured quantity to the total PM_{2.5} mass (filterable and condensable particulate). In this table, total condensable particulate has been subdivided into its respective organic and inorganic fractions for illustrative purposes. Inorganic condensable particulate has been further subdivided to show the amount of PM_{2.5} mass accounted for by sulfate.

Table 5-9. Speciation Profile for PM_{2.5} Measured by Method PRE-4/202 (Site Alpha).

Substance	Average Mass Fraction (1) (%)	Uncertainty (%)	95% Confidence Upper Bound (%)
Filterable PM _{2.5}	1.8	93	3.1
Total Condensible PM	98	76	155
Organic CPM	7.2	69	11
Inorganic CPM	90	78	144
- Sulfate (as SO ₄ ²⁻)	73	72	114

(1) Mass fraction is percent of total PM_{2.5} (filterable and condensible).

The data from Table 5-9 are shown in Figure 5-3. As can be seen from the figure, nearly all of the PM_{2.5} mass comes from CPM (98 percent). The large majority of CPM is contained in the inorganic fraction, which accounts for 90 percent of the total PM_{2.5} mass.

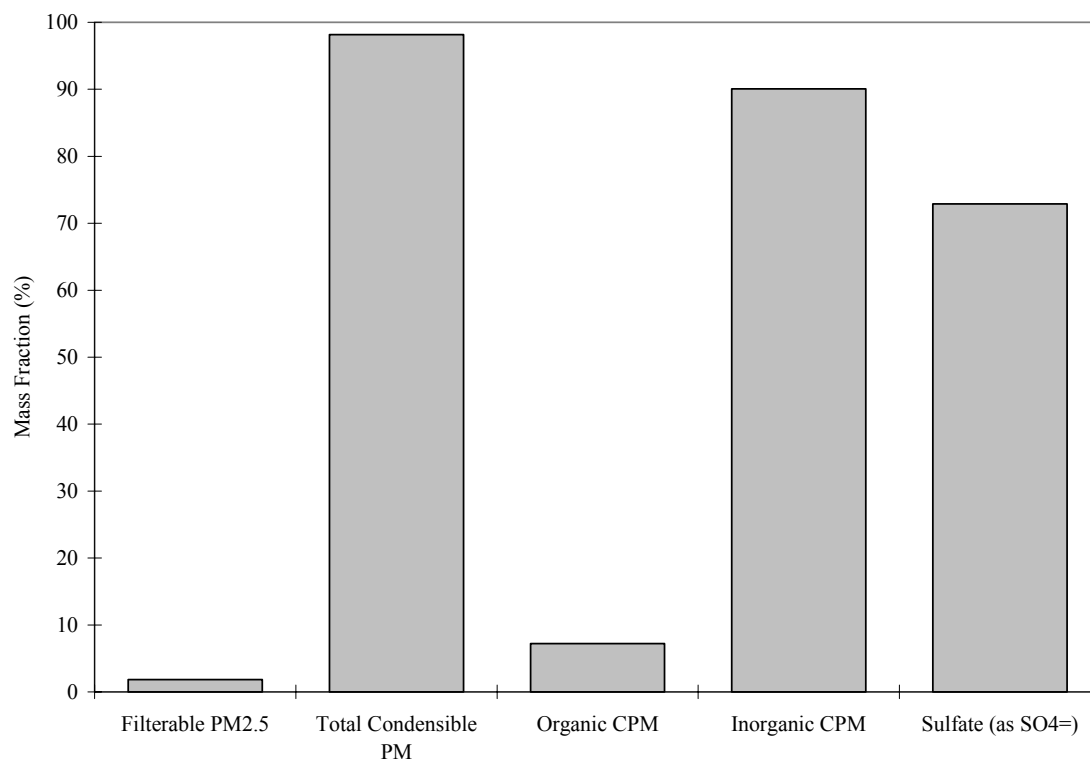


Figure 5-3. Method PRE-4/202 PM2.5 mass speciation profile (Site Alpha).

Section 6

QUALITY ASSURANCE

SAMPLE STORAGE AND SHIPPING

All samples requiring refrigeration were stored on-site in a refrigerator prior to shipment to the lab for analysis. In-stack (Method PRE-4) and impinger filters (Method 202) filters were stored in a desiccator at ambient conditions prior to shipment. All of the samples except the in-stack and impinger filters were shipped via overnight shipment to the lab in an ice chest with blue ice. Upon receipt of samples at the lab, those requiring refrigeration were stored at 4° C (nominal). Samples were stored and shipped in a manner to prevent breakage.

DILUTION SAMPLER FLOWS

Flow rates through the dilution sample collection media were determined by averaging the flow rates measured before testing commenced and after sampling was completed. The flow rates were measured by connecting a rotameter to each sampling media unit pre- and post-test and recording the flow; the rotameter was not in place during sampling. Results from the pre- and post-test flow checks are presented in Table 6-1. Pre- and post-test flow rates were generally consistent, with less than 10 percent variation. The Tenax and aldehyde samples had greater variation for some of the runs. Modifications to the equipment will allow for continuous monitoring of these flow rates so that they can be adjusted if varying too greatly from the original set point.

DILUTION SAMPLER QUALITY ASSURANCE SAMPLES

Field blank and ambient air quality assurance (QA) samples were collected and analyzed. A dilution sampler blank was not collected for this test series. A dilution sampler blank is collected by drawing filtered air through the dilution sampler and collecting samples per the normal procedures. Dilution sampler blank results are an indication of the background levels in the dilution sampler, likely from deposition of species on dilution sampler surfaces during sampling or HEPA and/or carbon filter breakthrough. Field blanks were collected by setting up and breaking down the dilution sampler sampling equipment without drawing gas through the sampling media. Field blank results are an indication of the species collected on the sampling

media during the handling and transport of the materials. Ambient air samples were collected by drawing air directly into the sampling media, bypassing the dilution sampler. The following tables present the results of the field blank and ambient air samples. The dilution sampler blank and field blank are presented as in-stack equivalents using the average dilution factor of the sampling runs. Ambient air samples are reported as measured. The average of the test series is also included in each table. Each blank is compared to the 95 percent confidence lower bound of the average. The procedures used for calculating the confidence intervals were described in Section 5. If the blank or ambient level is greater than the 95 percent lower bound the data is flagged. Flags suggest the field data may not be significantly different than the blank data. Further discussion on these results is presented in Section 7.

GRAVIMETRIC ANALYSIS

Dilution Sampler Filters

Prior to testing, unused filters were stored for at least one month in a controlled environment, followed by one week of equilibration in the weighing environment, to achieve stable filter tare weights. New and used filters were equilibrated at $20 \pm 5^\circ\text{C}$ and a relative humidity of 30 ± 5 percent for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro-microbalance with ± 1 microgram sensitivity. The electrical charge on each filter was neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance was calibrated with a 20 mg Class M weight and the tare was set prior to weighing each batch of filters. After every 10 filters were weighed, the calibration and tare were rechecked. If the results of these performance tests deviated by more than $\pm 5 \mu\text{g}$, the balance was recalibrated. If the difference exceeded $\pm 15 \mu\text{g}$, the balance was recalibrated and the previous 10 samples were reweighed. An independent technician checked 100 percent of initial weights and at least 30 percent of exposed weights; samples were reweighed if these check-weights did not agree with the original weights within $\pm 0.015 \text{ mg}$. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets, as well as being directly entered into a database via an RS232 connection.

Table 6-1. Pre- and Post-Test Flow Checks for the Dilution Sampler.

Run	Pre-test flow	Post-test flow	Average	% Difference
-----	---------------	----------------	---------	--------------

Teflon filter pack(scfh)

1	160	155	157.5	3%
2	160	160	160	0%
3	160	160	160	0%
4	160	160	160	0%
Ambient	160	160	160	0%

Quartz/citric acid filter pack (scfh)

1	160	165	162.5	-3%
2	160	165	162.5	-3%
3	160	165	162.5	-3%
4	160	165	162.5	-3%
Ambient	160	165	162.5	-3%

Quartz/potassium carbonate filter pack (scfh)

1	160	165	162.5	-3%
2	160	165	162.5	-3%
3	160	175	167.5	-9%
4	160	170	165	-6%
Ambient	160	170	165	-6%

PUF/XAD (scfh)

1	240	240	240	0%
2	240	240	240	0%
3	240	240	240	0%
4	240	240	240	0%
Ambient	240	240	240	0%

Tenax A (ml/min)

1	110	100	105	9%
2	110	100	105	9%
3	110	85	97.5	23%
4	110	80	95	27%
Ambient	110	95	102.5	14%

Tenax B (ml/min)

1	110	98	104	11%
2	110	90	100	18%
3	115	93	104	19%
4	110	110	110	0%
Ambient	110	85	97.5	23%

Aldehyde sampler (ml/min)

1	400	413	406.5	-3%
2	400	535	467.5	-34%
3	400	460	430	-15%
4	400	400	400	0%
Ambient	400	370	385	8%

Results from the dilution sampler field blank and ambient samples are presented in Table 6-2. The 95 percent lower confidence bound of average PM2.5 concentration from the stack samples was less than the ambient concentration.

Table 6-2. Dilution Sampler PM2.5 Blank Results (mg/dscm).

	mg/dscm			
	Average	DSB	FB	Ambient
PM2.5 mass	< 4.12E-2	e	ND	3.08E-2 c

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

In-Stack Filters

The balance was calibrated daily with two “S” type weights in the range of the media being weighed (5 and 10 g) and the tare was set prior to weighing each batch of filters. If the results of these performance tests had deviated by more than ± 1 mg, the balance would have been recalibrated. Performance test results were within specifications, thus recalibration was not required. If consecutive sample weights deviated by more than ± 0.5 mg, the sample was returned to the desiccator for at least 6 hours before reweighing. Pre- and post-weights, check weights and reweights (if required) were recorded on data sheets.

Table 6-3 presents the results of the methylene chloride, water and acetone rinse blanks. The acetone blank values were used to correct the EPA Method PRE-4 particulate data. Results of the filter blank weights are also presented in Table 6-3. All negative filter weights were treated as a zero in final calculations.

An analysis of the acetone rinse blanks is presented in Table 6-4. The particulate mass detection limit was calculated as three times the standard deviation of the results of the field blank acetone rinses and the acetone recovery blank. The resulting detection limit of approximately 1.1 mg further indicates that the filterable particulate levels at the heater were near detection limits.

Table 6-3. Filter and Reagent Blank Results.

Sample	Mass (mg)
Method 202 Water Recovery Blank (380 ml)	2.2
Method 202 Dichloromethane Recovery Blank (150 ml)	ND (1)
Method PRE-4 Acetone Recovery Blank (37 ml)	0.2
Impinger Filter Blank	0.4
Dilution Sampler Filter Blank	ND (2)

1- Detection limit = 1 mg

2- Detection limit of balance = 0.001 mg.

Table 6-4. Results from Acetone Blank Rinses.

Sample Fraction	Mass (mg)
PM10 cyclone catch rinse	0.2
PM2.5 cyclone catch rinse (2.5-10 μm)	1
<PM2.5 rinse (<2.5 μm)	0.8
Recovery Blank	0.2
Impinger Filter Blank	0.4
Detection Limit (3*standard deviation)	1.1

Therefore, the filterable particulate data from Method PRE-4 are presented in Section 5 for qualitative purposes only.

ELEMENTAL (XRF) ANALYSIS

Three types of XRF standards were used for calibration, performance testing and auditing: 1) vacuum-deposited thin-film elements and compounds (supplied by Micromatter, Deer Harbor, WA); 2) polymer films; and 3) National Institute of Standards and Technology (NIST) thin-glass films. The vacuum deposit standards cover the largest number of elements and were used as calibration standards. The polymer film and NIST standards were used as quality control standards. Standards from the NIST are the definitive standard reference material, but are only available for the species Al, Ca, Co, Cu, Mn, and Si (Standard Reference Material (SRM) 1832) and Fe, Pb, K, Si, Ti, and Zn (SRM 1833). A separate Micromatter thin-film standard was used to calibrate the system for each element.

A quality control standard and a replicate from a previous batch were analyzed with each set of 14 samples. When a quality control value differed from specifications by more than ± 5 percent

or when a replicate concentration differed from the original value (when values exceed 10 times the detection limits) by more than ± 10 percent, the samples were reanalyzed. If further tests of standards showed that the system calibration had changed by more than ± 2 percent, the instrument was recalibrated as described above. All XRF results were entered directly into the DRI databases.

Results from the field blank and ambient sample are presented in Table 6-5. Mg, Na and P were present at detectable levels in the field blank and were present at levels comparable to those in the stack samples. Only S was present in the stack samples at a concentration that was significantly different from levels in the ambient sample.

Table 6-5. XRF Elemental Analysis Field Blank Results (mg/dscm).

	mg/dscm				
	Average	DSB	FB	Ambient	
Al	6.58E-04	e	ND	4.62E-04	c
Br	< 2.29E-05	e	ND	4.25E-06	c
Ca	4.33E-04	e	ND	4.77E-04	c
Cd	< 3.48E-04	e	ND	ND	
Cl	< 4.98E-04	e	ND	1.71E-03	c
Cu	5.60E-04	e	ND	1.58E-05	c
Fe	2.98E-03	e	ND	8.42E-04	c
K	< 1.26E-04	e	ND	2.69E-04	c
Mg	4.09E-04	e	1.41E-04	1.31E-04	c
Na	8.07E-04	e	4.05E-04	6.01E-04	c
P	< 1.25E-04	e	9.86E-05	ND	
Pb	< 8.58E-05	e	ND	1.23E-05	d
S	1.11E-02	e	ND	4.44E-04	
Si	7.78E-04	e	ND	1.45E-03	c
Ti	< 6.20E-05	e	ND	7.64E-05	d
V	< 5.54E-05	e	ND	6.84E-06	d
Zn	< 2.26E-03	e	ND	3.79E-05	c

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

ORGANIC AND ELEMENTAL CARBON ANALYSIS

The TOR system was calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response was compared to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration were conducted at the beginning and end of each day's operation. Intervening samples were reanalyzed when calibration changes of more than ± 10 percent were found.

Known amounts of American Chemical Society (ACS) certified reagent-grade crystal sucrose and KHP were committed to TOR as a verification of the organic carbon fractions. Fifteen different standards were used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter were entered into the DRI database.

Organic carbon was present at detectable levels in the dilution sampler blank and field blank (Table 6-6). Elemental carbon was below its detection limit in the field blank.

Table 6-6. Field Blank and Ambient Results – OC/EC Analysis.

	mg/dscm			
	Average	DSB	FB	Ambient
OC	7.2E-02	e	5.1E-02	3.6E-03
EC	8.1E-03	e	ND	7.9E-04 c

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

SULFATE, NITRATE, AND CHLORIDE ANALYSIS

The primary standard solutions containing NaCl, NaNO₃ and (Na)₂SO₄ were prepared with reagent grade salts, that were dried in an oven at 105 °C for one hour and then brought to room temperature in a desiccator. These anhydrous salts were weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature (approximately 20 °C) and relative humidity (± 30 percent) conditions. These salts were diluted in precise volumes of DI

water. Calibration standards were prepared at least once within each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared were at 0.1, 0.2, 0.5, 1.0, and 2.0 µg/ml for each of the analysis species. Calibration curves were performed weekly. Chemical compounds were identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DI water blank was analyzed after every 20 samples and a calibration standard was analyzed after every 10 samples. These quality control checks verified the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards were used daily as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) were traceable to NIST simulated rainwater standards. If the values obtained for these standards did not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or ± 5 percent), the samples between that standard and the previous calibration standards were reanalyzed.

After analysis, the printout for each sample in the batch was reviewed for the following: 1) proper operational settings; 2) correct peak shapes and integration windows; 3) peak overlaps; 4) correct background subtraction; and 5) quality control sample comparisons. When values for replicates differed by more than ± 10 percent or values for standards differed by more than ± 5 percent, samples before and after these quality control checks are designated for reanalysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters are also designated for reanalysis.

Only NH_3 and Na^+ were detected in the field blank. Results of blanks and ambient samples are presented in Table 6-7. The ambient concentration of Cl^- is not significantly different than the in-stack average concentration.

SVOC ANALYSIS

Prior to sampling, the XAD-4 resin was Soxhlet extracted with methanol, followed by dichloromethane, each for 24 hours. The cleaned resin was dried in a vacuum oven heated to 40°C and stored in sealed glass containers in a clean freezer. The PUF plugs were Soxhlet

Table 6-7. Ions and Secondary PM Precursor Blank Results (mg/dscm).

	mg/dscm			
	Average	DSB	FB	Ambient
Cl-	< 2.53E-3	e	ND	1.90E-3 c
NO3-	6.76E-3	e	ND	5.64E-4
SO4=	2.88E-2	e	ND	1.35E-3
NH4+	< 1.36E-2	e	ND	2.92E-4
NH3	1.97E-1	e	1.26E-3	1.07E-3
SO2	2.71E+1	e	ND	8.67E-4
Soluble Na	2.66E-4	e	2.23E-4 b	6.60E-5

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

extracted with acetone, followed by 10 percent diethyl ether in hexane. The TIGF filters were cleaned by sonification in dichloromethane for 30 minutes followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and approximately 10 percent of the precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in hexane-rinsed aluminum foil and stored in a clean freezer prior to shipment to the field.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair:

naphthalene-d8	9.76	ng/μl	
acenaphthene-d8	10.95	ng/μl	(for acenaphthene and acenaphthylene)
biphenyl-d10	7.56	ng/μl	
phenanthrene-d10	4.61	ng/μl	
anthracene-d10	3.5	ng/μl	
pyrene-d10	5.28	ng/μl	(for fluoranthene and pyrene)
chrysene-d12	3.54	ng/μl	(for benz[a]anthracene and chrysene)
benzo[e]pyrene-d12	4.20	ng/μl	
benzo[a]pyrene-d12	4.68	ng/μl	
benzo[k]fluoranthene-d12	2.0	ng/μl	
benzo[g,h]perylene-d12	1.0	ng/μl	(for indeno[1,2,3-cd]pyrene, dibenzo[ah+ac]anthracene, benzo[ghi]perylene and coronene)

Calibration curves for the GC/MS/MID quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. NIST SRM 1647 (certified PAH), with the addition of deuterated internal standards and compounds not present in the SRM, was used to make calibration solutions. Three concentration levels for each analyte were employed, and each calibration solution was injected twice. After the three-level calibration was completed, a standard solution was injected to perform calibration checks. If deviation from the true value exceeded 20 percent, the system was recalibrated. The MSD was tuned daily for mass sensitivity using perfluorotributylamine.

In addition, one level calibration solution was run daily. If the difference between true and measured concentrations exceeded 20 percent, the system was recalibrated.

Results from the field blank are presented in Table 6-8. All average concentrations of compounds with a 95 percent confidence lower bound less than either the field blank or the ambient sample are flagged in the table.

VOC ANALYSIS

Calibration curves were performed weekly. Volatile organic compounds were identified by matching the response factors of each unknown sample with the response factors of the standards. Tenax cartridges spiked with a mixture of paraffinic (in the C9-C20 range) and aromatic (C4, C5, and C6 benzenes) hydrocarbons were periodically analyzed by GC/FID to verify quantitative recovery from the cartridges. Three to five different concentrations of the hydrocarbon (HC) standard and one zero standard were injected, and the response factors obtained. If the percent difference of the response factor from the mean was more than 5 percent, the response factors were corrected before proceeding with the analysis.

Results from the Tenax field blank are shown in Table 6-9. Almost all values in the stack samples are within an order of magnitude of the blank values. Results from the Canister ambient sample are shown in Table 6-10. Almost all values in the stack samples are more than an order of magnitude greater than the ambient levels.

Table 6-8. PUF/XAD Field Blank Results (mg/dscm).

Compound	NG-Average	DS Blank	Field Blank	Ambient
Naphthalene	< 4.2E-3	e	ND d	ND d
2-methylnaphthalene	3.9E-3	e	ND	7.8E-5
1-methylnaphthalene	1.8E-3	e	ND	3.7E-5
Biphenyl	< 1.8E-4	e	ND d	ND d
1+2-ethylnaphthalene	4.1E-4	e	ND	7.7E-6
2,6+2,7-dimethylnaphthalene	6.5E-4	e	ND	1.1E-5
1,3+1,6+1,7-dimethylnaphthalene	1.1E-3	e	ND	1.8E-5
1,4+1,5+2,3-dimethylnaphthalene	< 3.2E-4	e	ND	ND
A-trimethylnaphthalene	2.1E-4	e	ND	5.6E-6
1-ethyl-2-methylnaphthalene	7.7E-5	e	ND	1.8E-6
B-trimethylnaphthalene	1.6E-4	e	4.5E-6	4.1E-6
C-trimethylnaphthalene	1.8E-4	e	1.8E-5	4.4E-6
2-ethyl-1-methylnaphthalene	< 7.9E-4	e	ND	1.6E-5
E-trimethylnaphthalene	7.4E-5	e	ND	1.8E-6
2,3,5+1-trimethylnaphthalene	1.1E-4	e	ND	3.2E-6
J-trimethylnaphthalene	7.7E-5	e	5.0E-5 b	1.8E-6
Acenaphthylene	< 2.5E-4	e	ND	ND
Phenanthrene	1.1E-4	e	ND	4.0E-6
9-fluorenone	< 3.1E-4	e	ND	ND
2-methylphenanthrene	2.3E-5	e	5.4E-6	3.7E-7
Anthrone	< 5.7E-6	e	ND	7.5E-8 c
C-dimethylphenanthrene	< 1.9E-4	e	2.0E-4 b	9.0E-6
D-dimethylphenanthrene	< 6.4E-5	e	ND d	ND d
E-dimethylphenanthrene	< 8.9E-5	e	3.4E-5 d	ND d
Anthracene	< 2.7E-6	e	ND d	ND d
Fluoranthene	2.7E-5	e	2.8E-5 b	8.7E-7 c
Pyrene	< 1.6E-5	e	ND	4.0E-7 c
B-MePy/MeFl	< 9.1E-6	e	ND d	1.7E-7 d
C-MePy/MeFl	4.4E-5	e	1.2E-4 b	1.8E-6 c
D-MePy/MeFl	1.7E-5	e	3.1E-5 b	7.9E-7 c
Benz(a)anthracene	4.1E-4	e	1.1E-4 b	1.2E-5 c
7-methylbenz(a)anthracene	< 9.9E-5	e	2.3E-5 b	4.4E-6 c
Chrysene	< 1.7E-5	e	3.1E-5 b	3.2E-7 c
Benzanthrone	< 1.9E-5	e	2.8E-5 d	8.2E-7 d
5+6-methylchrysene	8.5E-6	e	1.9E-5 b	3.5E-7 c
Benzo(e)pyrene	< 5.1E-5	e	2.3E-5 d	ND d
Benzo(a)pyrene	< 1.5E-5	e	4.8E-5 d	4.5E-7 d

DS - Dilution Sampler

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

CARBONYLS ANALYSIS

Results from the Carbonyls field blank and ambient sample analyses are shown in Table 6-11.

Acetone was detected in the field blank at a concentration greater than the 95% confidence lower bound of the average concentration; none of the compounds were detected in the ambient sample at a concentration greater than the 95% confidence lower bound of the average stack concentration.

Table 6-9. Tenax Field Blank (mg/dscm).

Substance	mg/dscm					
	Average	DSB	FB		Ambient	
Benzaldehyde	2.2E-1	e	2.3E-2	b	3.9E-3	c
Hexadecanoic acid	1.9E-1	e	ND		1.1E-2	c
Styrene	9.2E-2	e	4.0E-2	b	7.5E-4	c
Acetophenone	8.1E-2	e	7.5E-3	b	2.1E-3	c
Phenol	3.9E-2	e	1.3E-2	b	8.2E-4	c
Nonanal	2.1E-2	e	4.8E-3	b	3.3E-4	c
Decanal	< 1.7E-2	e	1.5E-2	d	6.7E-4	d
m & p-xylene	1.4E-2	e	1.6E-3		8.9E-4	
Nonane	7.8E-3	e	1.9E-3	b	2.8E-4	
Ethylbenzene	6.3E-3	e	1.7E-3	b	2.8E-4	c
m & p-methylphenol	< 6.0E-3	e	2.9E-3	d	6.4E-5	d
Decane	5.4E-3	e	ND		2.1E-4	c
Biphenyl	5.1E-3	e	3.0E-3	b	1.0E-4	c
o-xylene	4.9E-3	e	ND		3.1E-4	
Heptanal	< 4.8E-3	e	ND	d	ND	d
Undecane	4.4E-3	e	1.5E-3	b	2.6E-4	
Dodecene	4.3E-3	e	5.1E-3	b	1.7E-4	c
1,2,4-trimethylbenzene	3.4E-3	e	ND		2.7E-4	c
m-ethyltoluene	3.3E-3	e	ND		1.9E-4	
1-undecene	3.2E-3	e	ND		7.8E-5	c
Naphthalene	3.0E-3	e	ND		8.4E-5	c
Dodecane	3.0E-3	e	ND		1.9E-4	
1-nonene	2.6E-3	e	2.6E-3	b	9.6E-5	
4-methylstyrene	< 2.6E-3	e	ND	d	ND	d
2,3-benzofuran	2.5E-3	e	ND		5.5E-5	c
1,3-dichlorobenzene	2.0E-3	e	ND		7.3E-5	
Pentadecane	< 1.9E-3	e	ND	d	ND	d
C-dimethylindane	1.8E-3	e	ND		9.2E-5	
2-heptanone	< 1.6E-3	e	ND	d	ND	d
p-ethyltoluene	< 1.5E-3	e	ND	d	1.2E-4	d
Tetradecane	1.5E-3	e	ND		5.1E-5	
Propylbenzene	< 1.4E-3	e	ND	d	5.9E-5	d
1,3,5-trimethylbenzene	< 1.3E-3	e	ND	d	6.1E-5	d
Indene	< 1.0E-3	e	ND	d	ND	d
o-ethyltoluene	< 9.8E-4	e	ND	d	8.1E-5	d
2-methylnaphthalene	< 9.5E-4	e	ND	d	4.5E-5	d

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

Table 6-10. Canister Samples VOC's Blanks Results (Site Alpha).

Substance	mg/dscm			
	Average	DSB	Ambient	
Propene	2.3E+0	e	5.2E-3	
n-butane	1.3E+0	e	3.3E-3	
Propane	9.9E-1	e	5.5E-3	
Isobutane	6.5E-1	e	3.1E-3	
Cyclohexane	4.3E-1	e	2.4E-4	c
Ethane	4.0E-1	e	3.1E-3	
1-decene	2.7E-1	e	3.2E-3	
Ethene	2.3E-1	e	8.2E-4	c
n-hexane	1.8E-1	e	7.6E-4	c
Isopentane	1.7E-1	e	2.8E-3	
2,3,5-trimethylhexane	1.6E-1	e	3.0E-3	
Acetylene	1.1E-1	e	1.0E-3	
Toluene	8.3E-2	e	2.6E-3	
Methanol	8.3E-2	e	5.8E-4	c
Iso-butene	7.9E-2	e	7.1E-4	
1-butene	7.6E-2	e	5.7E-4	
Methylcyclopentane	6.0E-2	e	6.5E-4	c
c-2-butene	5.5E-2	e	1.9E-4	
t-2-butene	5.4E-2	e	3.8E-4	
Acetone	4.4E-2	e	6.7E-4	c
n-pentane	4.1E-2	e	1.2E-3	
Benzene	2.2E-2	e	6.8E-4	
Nonanal	2.0E-2	e	1.9E-3	c
2-methylpentane	1.9E-2	e	9.4E-4	
1-pentene	1.9E-2	e	5.6E-4	
m- & p-xylene	1.7E-2	e	1.3E-3	
3-methylpentane	1.7E-2	e	6.0E-4	c
Octanal	1.5E-2	e	9.8E-4	
Hexanal	1.4E-2	e	4.9E-4	
Styrene + heptanal	1.2E-2	e	4.8E-4	
Cyclopentane	1.1E-2	e	1.8E-4	
1,3-diethylbenzene	8.9E-3	e	1.0E-4	
1-hexene	8.7E-3	e	2.3E-4	c
t-2-pentene	7.9E-3	e	1.4E-4	
2,2,5-trimethylhexane	< 7.7E-3	e	ND	d
n-decane	7.6E-3	e	2.1E-4	
3-methylhexane + pentanal	7.5E-3	e	4.5E-4	
n-undecane	7.4E-3	e	2.7E-4	
o-xylene	7.3E-3	e	4.8E-4	
2,2,4-trimethylpentane	7.2E-3	e	6.8E-4	
C10 olefin 2	7.0E-3	e	1.2E-5	
2-methyl-1-butene	7.0E-3	e	6.4E-4	
2-methyl-2-butene	6.8E-3	e	1.7E-4	c
n-heptane	6.7E-3	e	3.6E-4	
Methylcyclohexane	6.5E-3	e	3.3E-4	
2,3-dimethylbutane	6.4E-3	e	3.4E-4	
C10 paraffin C	5.8E-3	e	3.6E-5	
1,2,4-trimethylbenzene	5.8E-3	e	3.0E-4	
C10 paraffin A	5.6E-3	e	7.8E-5	
2-methylhexane	5.3E-3	e	3.5E-4	
m-ethyltoluene	5.1E-3	e	3.3E-4	
Isobutylbenzene	5.0E-3	e	5.1E-5	
n-dodecane	4.7E-3	e	1.1E-4	
MTBE	< 4.5E-3	e	1.1E-4	c

Table 6-10. Canister Samples VOC's Blanks Results (Site Alpha) (Continued).

Substance	mg/dscm			
	Average	DSB	Ambient	
3,6-dimethyloctane	4.4E-3	e	9.6E-5	
Ethylbenzene	4.4E-3	e	3.0E-4	
3-methyl-1-butene	4.4E-3	e	4.1E-5	
c-2-pentene	4.3E-3	e	7.7E-5	
2,3-dimethylpentane	4.1E-3	e	4.5E-4	
n-octane	3.6E-3	e	1.6E-4	
2,2-dimethylbutane	3.6E-3	e	1.6E-4	
2,6-dimethyloctane	3.6E-3	e	7.2E-5	
2,4-dimethylpentane	3.5E-3	e	2.3E-4	
1,3-dimethylcyclopentane	3.4E-3	e	1.5E-4	
1,4-diethylbenzene	3.3E-3	e	2.0E-4	
1,2,3,5-tetramethylbenzene	3.2E-3	e	4.0E-5	
3-ethylpentane	3.1E-3	e	1.7E-4	
2,3,-trimethylpentane	2.7E-3	e	2.8E-4	
n-nonane	2.5E-3	e	1.6E-4	
p-ethyltoluene	2.5E-3	e	1.6E-4	
n-propylbenzene	2.5E-3	e	1.2E-4	
1,2-diethylbenzene	2.4E-3	e	1.1E-4	
Cyclopentene	2.4E-3	e	1.7E-5	
2-methylheptane	2.4E-3	e	1.7E-4	
Heptene-1	< 2.4E-3	e	ND	
1,3,5-trimethylbenzene	2.4E-3	e	1.8E-4	
2,4,4-trimethyl-1-pentene	2.3E-3	e	4.1E-5	
beta-pinene	2.3E-3	e	5.7E-5	
Naphthalene	2.3E-3	e	5.9E-5	
Ethanol + ACN	< 2.1E-3	e	ND	d
o-ethyltoluene	2.1E-3	e	9.0E-5	
1,3-butadiene	2.0E-3	e	1.3E-4	
C8 olefin 3	1.9E-3	e	1.2E-5	
3-methylheptane	1.9E-3	e	1.4E-4	
1,2,3,4-trimethylbenzene	1.8E-3	e	7.3E-5	
1,2,4,5-tetramethylbenzene	1.6E-3	e	2.8E-5	
1,2,3-trimethylbenzene	1.6E-3	e	2.8E-5	c
t-2-hexene	1.6E-3	e	4.1E-5	
C10 aromatic 5	1.5E-3	e	4.0E-5	
2,5-dimethylhexane	1.5E-3	e	7.8E-5	
C8 paraffin 2	1.5E-3	e	6.6E-5	
3-methyloctane	1.4E-3	e	1.8E-5	
c-3-hexene	1.3E-3	e	1.2E-5	
2-methyl-2-pentene	1.2E-3	e	4.1E-5	
t-3-hexene + chloroform	< 1.2E-3	e	1.8E-5	c
2,5-dimethylheptane	1.2E-3	e	6.0E-5	
C9 olefin 3	1.2E-3	e	5.3E-5	c
Octene-1	1.2E-3	e	5.3E-5	
Isopropyltoluene	1.1E-3	e	1.7E-5	
1,1-dimethylcyclohexane	1.1E-3	e	4.7E-5	c
Indan	1.1E-3	e	7.2E-5	

Table 6-10. Canister Samples VOC's Blanks Results (Site Alpha) (Continued).

Substance	mg/dscm		
	Average	DSB	Ambient
C10 aromatic 2	1.1E-3	e	6.2E-5
1-methylcyclopentene	1.1E-3	e	2.3E-5
C10 aromatic 6	1.0E-3	e	1.1E-5
1-methylindan	< 1.0E-3	e	1.1E-5
c-2-hexene	< 1.0E-3	e	ND
Isopropylcyclohexane	9.7E-4	e	5.9E-5
trans-3-methyl-2-pentene	9.7E-4	e	4.1E-5
Indene	8.4E-4	e	2.7E-5
C11 aromatic 1	< 8.3E-4	e	1.7E-5
3,3-dimethylpentane	8.2E-4	e	3.6E-5
C9 paraffin 1	8.2E-4	e	3.0E-5
2,6-dimethylheptane	8.2E-4	e	3.6E-5
2,3-dimethylhexane	8.2E-4	e	1.2E-5
2-methyl-1-pentene	8.1E-4	e	2.4E-5
t-3-heptene	< 7.9E-4	e	3.0E-5
C10 aromatic 1	7.7E-4	e	2.3E-5
4-methylheptane	7.6E-4	e	6.6E-5
4,4-dimethylheptane	7.6E-4	e	5.4E-5
C9 olefin 1	7.5E-4	e	2.4E-5
C8 olefin 1	7.5E-4	e	3.5E-5
cis-3-methyl-2-pentene	7.5E-4	e	2.4E-5
C6 olefin	7.5E-4	e	1.2E-5
C9 olefin 4	7.0E-4	e	ND
Limonene	6.8E-4	e	5.2E-5
C11 paraffin A	< 6.5E-4	e	2.4E-5
C7 olefin 1	< 6.5E-4	e	1.8E-5
Isopropylbenzene	5.6E-4	e	4.5E-5
3,3-dimethylheptane	5.5E-4	e	3.0E-5
C8 paraffin 3	< 4.4E-4	e	1.2E-5
C9 paraffin 3	4.4E-4	e	2.4E-5
Dodecene-1	< 4.3E-4	e	ND
4-methylhexene	4.3E-4	e	1.8E-5
Nonene-1	< 4.3E-4	e	1.8E-5
C7 olefin 2	< 4.3E-4	e	5.9E-6
Cyclohexene	4.2E-4	e	2.3E-5
C10 aromatic 4	4.1E-4	e	2.3E-5
Benzaldehyde	< 3.9E-4	e	5.1E-5
Chlorobenzene	3.6E-4	e	1.6E-5
sec-butylbenzene	< 3.1E-4	e	5.7E-6
C9 paraffin 2	2.7E-4	e	1.8E-5
2,4-dimethylhexane	2.2E-4	e	1.8E-5
C8 olefin 2	< 2.1E-4	e	5.9E-6
Total Identified NMHC	7.9E+0	e	5.4E-2
Unidentified	3.7E-1	e	7.1E-3

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the DSB concentration.

c - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

d - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

e - QA/QC sample not collected

Table 6-11. Carbonyls VOC's Blanks Results (Site Alpha).

Substance	mg/dscm			
	Average	DSB	FB	Ambient
Formaldehyde	7.2E-2	d	ND	1.5E-3
Acetaldehyde	7.6E-2	d	1.4E-2	1.8E-3
Acetone	1.5E+0	d	2.7E+0	4.0E-2
Glyoxal	1.8E-2	d	ND	6.0E-4

DSB - Dilution Sampler Blank

FB - Field Blank

a - 95% Confidence Lower Bound of the Average concentration is less than the FB concentration.

b - 95% Confidence Lower Bound of the Average concentration is less than the Ambient concentration.

c - Insufficient data to calculate 95% Confidence Lower Bound of the Average concentration.

d - QA/QC sample not collected

INORGANIC RESIDUE ANALYSIS

A reagent blank was analyzed in the same manner as the field samples, as described in Section 3.

The results are presented in Table 6-12. Al, Cr, Cu, Fe, Mn, Mo, Ni, Sulfate, and Zn are the only compounds with stack concentrations more than an order of magnitude greater than the equivalent reagent blank concentration.

Table 6-12. Method 202 Water Reagent Blank Results (mg/dscm).

Compound	mg/dscm	Compound	mg/dscm
Fluoride	8.00E-03	Mg	< 3.20E-03
Chloride	1.20E-02	Mn	< 1.40E-04
Nitrate (as N)	8.50E-02	Mo	1.40E-04
Sulfate (as SO4=)	< 9.50E-03	Ni	< 5.50E-04
Ammonium (as NH4+)	ND	P	< 1.60E-03
Al	< 8.20E-04	K	< 2.70E-02
Ba	< 2.70E-05	Si	5.20E-03
Be	< 2.70E-05	Ag	< 2.70E-04
B	1.60E-03	Na	1.60E-01
Cd	< 5.50E-05	Sr	2.40E-04
Ca	5.00E-02	Tl	< 1.60E-03
Cr	< 1.10E-04	Sn	< 1.40E-03
Co	< 2.70E-04	Ti	< 2.70E-04
Cu	< 1.60E-04	V	< 2.70E-04
Fe	< 5.50E-04	Zn	< 2.70E-04
Pb	< 5.50E-04	Zr	< 2.70E-04

< - below limit of quantitation (Detection limit x 3.33)

ND - not detected

Section 7

DISCUSSION AND FINDINGS

The objectives of this test were to develop emissions factors and speciation profiles for particulate emissions, including PM_{2.5}, as well as gaseous secondary PM_{2.5} precursors. In addition to using the dilution sampler, samples were also collected according to EPA Method PRE-4/202. Before discussing the results, it is instructive to review the differences between these procedures.

The dilution sampler is designed to capture filterable PM and any aerosols that condense under simulated stack plume conditions. The sample gas is cooled to ambient temperatures, typically 60-70 °F in these tests, as it mixes with the dilution air in the dilution sampler. Samples for analyses are then collected from the diluted sample. Conventional in-stack methods are intended to collect particles that are filterable at the filter temperature and those that condense in a series of aqueous impingers placed in an ice bath. The gas temperature leaving the impingers is typically 55-65 °F; thus, both systems cool the sample gas to similar final temperatures. However the in-stack methods cool the sample rapidly without dilution by quenching the gas sample in water maintained at near freezing temperatures, while the dilution sampler cools and dilutes the sample more slowly by mixing it with purified ambient air. Since aerosol condensation depends on temperature, concentration, residence time and other factors, it is not surprising that the results of the two methods differ. However, mechanistic variations alone may not account for the magnitude of the difference observed in these tests.

DILUTION SAMPLER MEASUREMENTS

Filterable PM_{2.5} measured by the in-stack filter and cyclones (4.4×10^{-4} lb/MMBtu) is almost an order of magnitude higher than the dilution sampler value of 5.2×10^{-5} lb/MMBtu (Table 7-1). The low uncertainty of the dilution sample emission factor results from the very low standard deviation of the four runs.

Table 7-1. PM Emission Factor Comparison.

	Emission Factor (lb/MMBtu)	Uncertainty (%)	lb/hr	RSD (%)
Dilution Sampler: Filterable PM<2.5	5.23E-5	43	0.00858	17
EPA PRE-4/202 (in-stack filter)				
Filterable PM (all sizes)	8.89E-4 *	89	0.147	54
Filterable PM<2.5	4.36E-4 *	76	0.0716	48
Condensable PM (Unpurged Train)	7.77E-3 *	93	1.26	60
Total PM2.5 (FPM2.5 + CPM)	8.20E-3 *		1.33	

* Emission factors not recommended for emission estimation purposes.

Particulate OC

There is currently heightened interest in particulate carbon from gas-fired combustion sources due to PM₁₀ and PM_{2.5} NAAQS and Regional Haze rules. Background work for development of PM_{2.5} State Implementation Plans has begun in several states in response to the 1997 PM_{2.5} NAAQS. In addition, atmospheric visibility is a key concern in Class 1 Areas, such as near National Parks. The National Park Service (NPS) must evaluate the visibility impact of new plants within 100 km of Class 1 Areas during permitting. Source emissions are evaluated for impact on regional haze and other criteria. Primary EC and OC, SO₄⁼ and NO₃⁻ aerosols, and coarse (PM_{10-2.5}) and fine (PM_{2.5}) PM emissions are key factors in the visibility evaluation. Quartz filters were used to collect PM that was then analyzed for OC and EC by TOR using the IMPROVE protocol. Previous studies have shown that OC measurements on quartz filters are susceptible to biases: adsorption of VOCs onto the filter media and collected PM, and devolatilization of organic PM, with the adsorptive effect dominating and causing a positive bias (Winegar, 1993). In these tests, a quartz fiber filter was placed downstream of a TMF during sample collection and subsequently analyzed for OC and EC to determine the extent of this bias (Turpin, 1994). The OC collected on this filter may be used to evaluate the potential significance of the adsorption bias relative to the OC collected on the front-loaded quartz fiber filter. This is commonly referred to as “backup OC”. In some cases, this approach may overestimate the extent of the bias because the adsorptive capacity of the filter media itself and the collected particles can affect the amount of VOC adsorbed on the filter (Kirchstetter, 2001). Therefore, it is convention not to correct OC measurements for the backup filter/bias results, but rather to present both sets of results and discuss the potential impact of the bias on the measured OC results.

Table 7-2 presents the data from the backup and front quartz filters used this test, as well as the equivalent OC concentration if the results are corrected for backup OC (i.e., the OC mass measured on the backup quartz filter is subtracted from the OC mass measured on the primary quartz filter). For this test, the backup OC ranged from 78 to 124 percent of the OC concentration measured on the primary quartz filter. These results are qualitatively similar to the results of Hildemann et al. (1991), who determined speciated PM emissions from gas-fired home appliances using methods identical to those used in this program. Hildemann found that OC accounted for 84.9 percent of PM mass and that the backup OC accounts for 73 percent of the measured OC emissions, on average. Hildemann's data are incorporated into EPA's SPECIATE database, and are currently the only PM speciation data available for gas-combustion. Thus, Hildemann's results provide validation of the OC results measured in this study, and also reinforce the need for caution when using the OC results.

Table 7-2. Organic Carbon and Backup Filter Organic Carbon Results (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average	FB	Ambient
OC	0.0776	0.0695	0.0689	0.0728	0.0722	0.0505	0.0036
Backup Filter OC	0.0862	0.0540	0.0854	0.0777	0.0758	0.0251	0.0017
OC - Corrected for Backup Filter OC	-0.0086	0.0155	-0.0165	-0.0049	-0.0036	0.0255	0.0018
Backup Filter OC/OC	111.1	77.7	124.0	106.7	104.9	49.6	48.2

Figure 7-1 shows the potential impact of the bias on the overall average sample concentration, and the levels in the field blank. Although the ambient result appears to be elevated above the stack samples, the data are presented in mass per sample and the OC results from the stack sample results have not been corrected for dilution ratio in this graph. The high blank levels as well as the VOC adsorption associated with the quartz filters used to measure OC indicate a significant positive bias on the OC concentrations. In all runs, the corrected OC result is at or below the analytical detection limit. This result indicates that the true carbon emissions are probably below measured results and that they are too low to measure with high confidence, even when using these state-of-the art techniques. Therefore, the OC results should be considered as an upper bound for the potential OC emissions, with significant uncertainty beyond the reported values.

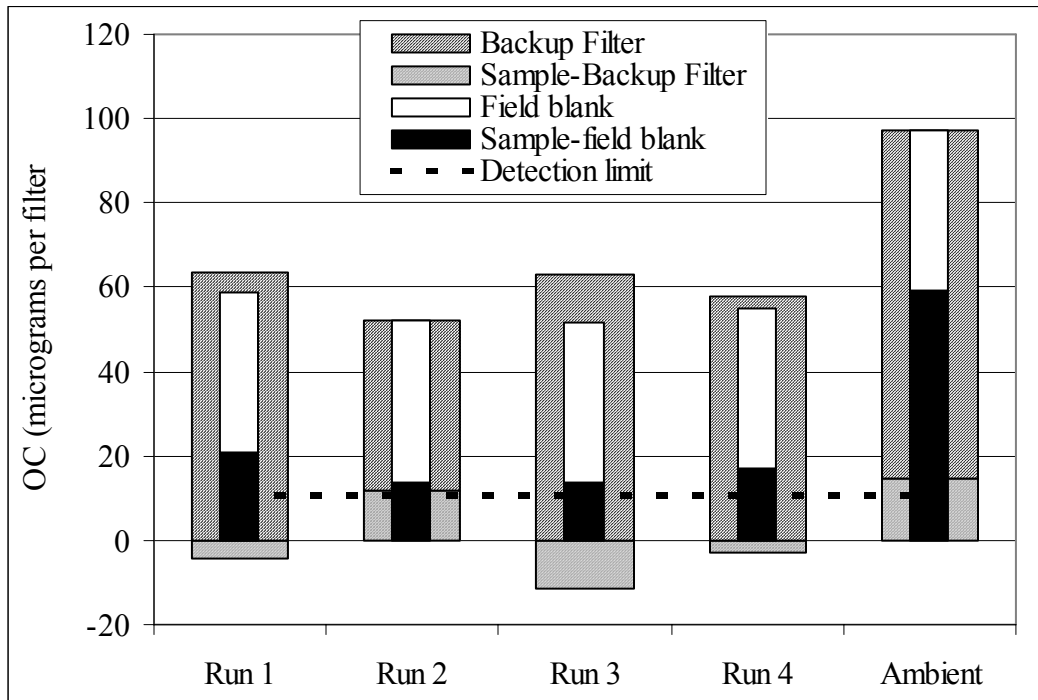


Figure 7-1. Site Alpha (Refinery Gas-Fired Process Heater) OC Results.

SULFATE COMPARISON

Dilution Sampler versus Method 202

Table 7-3 presents a comparison of the sulfur measurements, expressed as $\text{SO}_4^{=}$ in mg/dscm. The levels in the impinger aliquot from the purged train are approximately an order of magnitude greater than those from the unpurged train. The levels in the unpurged train are more consistent with previous tests of gas-fired units. The $\text{SO}_4^{=}$ measured in the purged Method 202 aliquot accounts for approximately 75 percent of the SO_2 (as $\text{SO}_4^{=}$) measured by the potassium carbonate-impregnated cellulose-fiber filter downstream of the dilution sampler. In turn, the SO_2 measured by the dilution sampler accounts for approximately half of the sulfur from the fuel gas. Compared to the measured SO_2 value, the $\text{SO}_4^{=}$ levels measured by the dilution sampler quartz filter account for approximately 0.06 percent of the SO_2 in the flue gas and are more than an order of magnitude greater than those measured in the ambient sample. Historical data of SO_2 concentrations from monitoring stations in the general sampling area show much lower levels of SO_2 , with a maximum concentration of 0.012 ppm for the area versus the one-day sample value of 7 ppm. This difference indicates a potentially higher concentration of SO_2 was present at the refinery site than was experienced in the surrounding area.

Table 7-3. Comparison of Sulfate Measurements (mg/dscm).

	Run 1	Run 2	Run 3	Run 4	Average
Impinger aliquot (M202) – purged	19	11	11	15	14
Impinger aliquot (M202) – unpurged	1.7	0.38	1.6	1.2	1.2
Dilution sampler $\text{SO}_4^{=}$ (IC)	0.018	0.034	0.014	0.050	0.029
Dilution sampler S (as $\text{SO}_4^{=}$) (XRF)	0.022	0.038	0.015	0.059	0.033
Dilution sampler SO_2 (as $\text{SO}_4^{=}$) (K_2CO_3 filter)	31	46	40	47	41
Ambient (1)	0.0014	--	--	--	0.0014
Total reduced sulfur in fuel (as $\text{SO}_4^{=}$)	46	77	55	59	59

(1) One ambient sample taken on separate day.

Artifact Sulfate Formation in the Impingers

The formation of artifact $\text{SO}_4^{=}$ caused by SO_2 absorption in the aqueous solutions appears likely. Both SO_2 and oxygen are soluble in water and the dissolved H_2SO_3 can slowly oxidize to $\text{SO}_4^{=}$. This reaction is implicitly recognized by Method 202, which recommends purging the impingers with nitrogen (air is also acceptable) to minimize this bias. Method 202 also provides the option of omitting the post test purge if the pH of the impingers is above 4.5; while the pH of the impingers met this criterion in our test, we performed the nitrogen purge anyway. However, earlier studies of systems having SO_2 levels of approximately 2000 ppm show that that these artifacts occur in spite of post-test purging (Filadelfia and McDaniel, 1996).

In the absence of any documented reports to evaluate artifact formation at low SO_2 concentrations, a laboratory scale study was conducted in a prior program evaluating potential bias at these concentrations (Wien et al., 2001). The experiments passed simulated combustion gas containing representative amounts of O_2 , CO_2 , N_2 , NO_x , and SO_2 through Method 202 impinger trains. No condensable substances were added. Tests were performed both with and without post-test nitrogen purges for 1-hour and 6-hour sampling runs for mixtures containing 0, 1, and 10 ppm SO_2 .

Significant amounts of $\text{SO}_4^{=}$, proportional to the SO_2 concentration in the gas, were found to be present in impingers that had not been purged. However, while the post-test purge definitely reduced the $\text{SO}_4^{=}$ concentrations it did not eliminate artifact formation. Purging was less efficient for the 6-hour runs relative to the 1-hour runs, indicating that most of the SO_2 oxidation occurs within this period. This result shows that the $\text{SO}_4^{=}$, and hence most of the CPM collected

by Method 202 in our field test results can come from this mechanism of artifact SO_4^- formation from dissolved SO_2 .

COMPARISON OF PURGED AND UNPURGED METHOD 202 TRAIN DATA

The paired purged and unpurged train results are completely opposite from the results of previous tests and are not readily explained. A review of those data led us to suspect the validity of the conventionally obtained CPM results and initiate a more extensive analysis of this fraction in this study than that prescribed by Method 202. Most of the inorganic CPM mass for both the purged and unpurged trains is composed of SO_4^- and NH_4^+ , with small contributions from Na and Ca (Figure 7-2). When all species are summed, the total mass exceeds the inorganic CPM mass for both the purged (109 percent of inorganic CPM) and the unpurged (130 percent of inorganic CPM) trains. The large SO_4^- content is expected since the sulfur content of the fuel gas is moderate (3 ppmv H_2S , with a total reduced sulfur content of 200 ppm as H_2S). SO_2 stack emissions measured by the dilution sampler averaged approximately 7 ppm. The extensive instrumental analysis (discussed in Section 4) of the impinger solutions does not find any significant levels of other metals. Although the difference of the measurements from the two Method 202 trains is an order of magnitude, the speciation of each train is similar, as seen in the two pie charts. This similarity yields no definitive species that can be attributed as the source of the difference in results.

To determine the repeatability of these anomalous results, the experiment of sampling two Method 202 trains side by side and purging one while leaving the other unpurged was recreated on a pilot scale facility firing natural gas. Two sets of paired Method 202 trains were run for two separate runs; one train from each set was purged while the second train remained unpurged. The results, presented in Table 7-4, along with other results from previous tests, show that the data obtained at Site Alpha for the purged train are not consistent. The data from the purged trains shown in Table 7-4 are lower than the unpurged trains at a 92 percent confidence level. As a result of these pilot scale tests, the previous field tests and the lab scale study described below, it is believed that the data for the unpurged trains for Site Alpha should be used in comparisons and are more representative than the data from the purged trains.

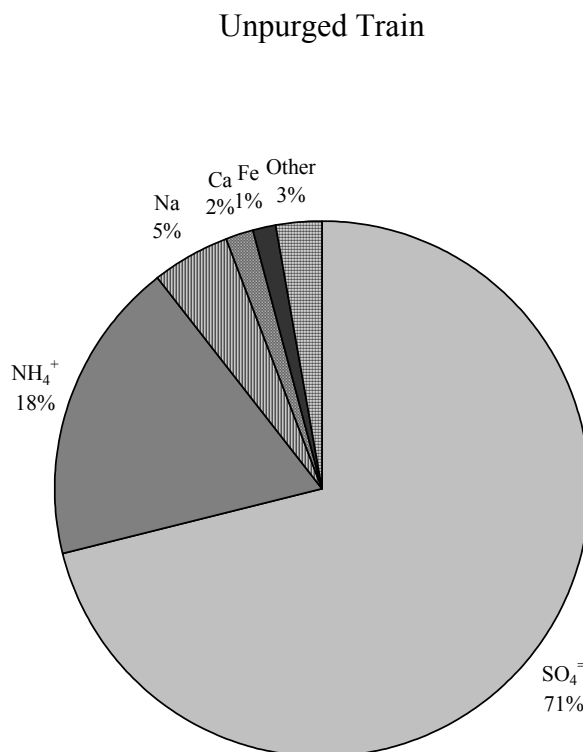
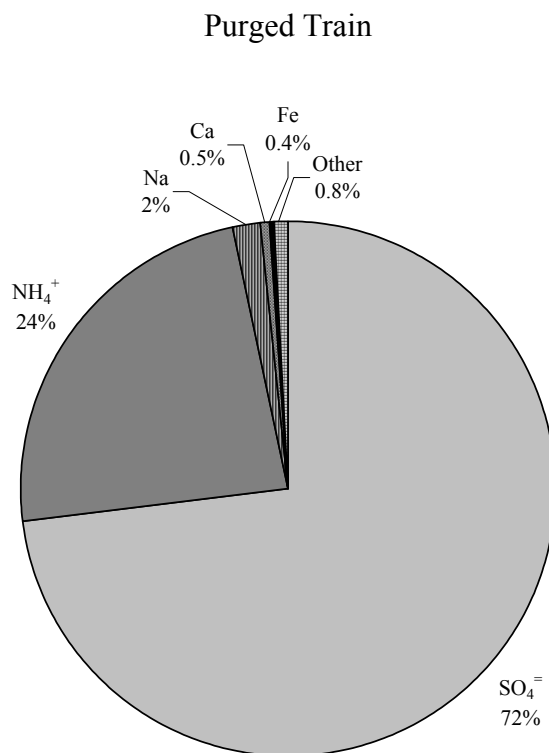


Figure 7-2. Inorganic CPM Residue Speciation Results.

Table 7-4. Results from Pilot Scale Evaluation of Purged versus Unpurged Method 202 Trains (mg/dscm).

	Average - Purged	Average - Unpurged
Inorganic CPM	2.10	3.09
Organic CPM	0.20	0.31
Sulfate - aliquot	8.37	11.29
Sulfate - residue	3.31	4.10
Ammonium - residue	0.78	1.06

COMPARISON TO PUBLISHED DATA

Corio and Sherwell (2000) reviewed emissions data collected from fossil fuel fired units by Method 201A/202 and noted the potential significance of artifact formation. Table 7-5 presents some of their data (Lakewood Cogeneration and Kamite Milford units) along with data collected in the current program (for DOE/CEC/NYSERDA/GRI/API) for gas-fired sources (Site Alpha) and its predecessor conducted for API/DOE/GRI (Sites A, B, C). These data compare results from the filterable and condensable PM fractions, along with the composition of CPM, for a natural gas-fired boiler and several natural gas-fired turbines.

As can be seen in Table 7-5, 93 percent of the total PM mass found by Method PRE-4/202 was contained in the condensable fraction collected in the impingers. This finding is similar to that from earlier tests of gas-fired units (England et al., 2000). The filterable fraction is comparable to the other refinery gas-fired process heater (Site B) tested as part of the previous API/DOE/GRI program.

The PM emission factors obtained using the Method PRE-4/202 trains are in general agreement with those found in the EPA's AP-42 emission factor database (EPA, 1998) for natural gas-fired external combustion devices (Table 7-6). Since the EPA results were obtained using the same method, a similar bias is likely in those data. The condensable catch from the unpurged train is slightly higher for this test (Site Alpha) than that reported in AP-42 (0.0078 versus 0.0056 lb/MMBtu in AP-42). The general agreement of our results with those presented in the EPA database provides additional confidence in the validity of the results found here.

Table 7-5. Comparison of Data from Corio and Sherwell (2000) and Current Program.

Source ¹	Unit Type	Filterable PM		Condensable PM		Makeup of CPM			
						Inorganic Fraction		Organic Fraction	
		lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total PM10	lb/ MMBtu	% of Total CPM	lb/ MMBtu	% of Total CPM
Lakewood Cogeneration	Natural Gas-fired Boiler	0.0019	46	0.0022	54	0.0015	66	0.00076	34
Lakewood Cogeneration – Unit #1	Natural Gas-fired Turbine	0.00021	14	0.0012	86	0.001	81	0.00023	19
Lakewood Cogeneration – Unit #2	Natural Gas-fired Turbine	0.00052	33	0.0011	67	0.00084	78	0.00024	22
Kamine Milford ²	Natural Gas-fired Turbine	0.0132	56	0.011	44	0.0045	43	0.006	57
Kamine Milford ³	Natural Gas-fired Turbine	0.0015	12	0.011	88	0.0067	60	0.0045	40
Kamine Milford ⁴	Natural Gas-fired Turbine	0.0012	10	0.011	90	0.0079	74	0.0028	26
Kamine Milford ⁵	Natural Gas-fired Turbine	0.0014	12	0.010	88	0.0066	66	0.0034	34
Site A	Refinery Gas-fired Boiler	0.00016	2	0.0097	98	0.0091	94	0.00064	6
Site B	Refinery Gas-fired Process Heater	0.00064	12	0.0046	88	0.0044	96 ⁽⁶⁾	0.00014	3 ⁽⁶⁾
Site C	Natural Gas-fired Steam Generator	0.000077	6	0.0012	94	0.00052	44 ⁽⁶⁾	0.00048	41 ⁽⁶⁾
Site Alpha	Refinery Gas-fired Process Heater	0.00059	7	0.0078	93	0.0066	86 ⁽⁶⁾	0.0011	14 ⁽⁶⁾

¹ Lakewood and Kamine Milford data collected with EPA Methods 201/201A and 202; data from Sites A-C, Alpha, Bravo and Charlie collected using EPA Methods PRE-4 and 202.

² Steam injection (SI) on, waste heat recovery boiler (WHRB) off.

³ SI off, WHRB off.

⁴ SI on, WHRB on.

⁵ SI off, WHRB on.

⁶ Remaining CPM mass accounted for by back-half filter and was not characterized.

Table 7-6. Comparison of EPA AP-42 Database and Current Program Data.

Source	Unit Type	Total PM10 (1)	Filterable PM		Condensable PM		PM2.5 by DT (2)
			lb/MMBtu	% of Total PM10	lb/MMBtu	% of Total PM10	
AP-42	Natural Gas Combustion	0.0075	0.0019	25	0.0056	75	--
Site A	Refinery Gas-fired Boiler	0.0099	0.000160	2	0.0097	98	0.00036
Site B	Refinery Gas-fired Process Heater	0.0052	0.00064	12	0.0046	88	0.000054
Site C	Natural Gas-fired Steam Generator	0.0013	0.000077	6	0.0012	94	0.000056
Site Alpha	Refinery Gas-fired Process Heater	0.0084	0.00059	7	0.0078	93	0.000052

(1) Data collected using EPA Method PRE-4/202 train.

(2) Data collected using dilution tunnel method; data presented is for PM<2.5 microns and includes filterable and condensable PM.

These results show that traditional source testing methods, such as EPA Method 202, probably overestimate particulate mass emissions by erroneously creating CPM, especially $\text{SO}_4^{=}$, that does not occur in the actual exhaust from the plant. $\text{SO}_4^{=}$ formed in the stack and $\text{SO}_4^{=}$ formed within the sample collection system are indistinguishable as a result of this $\text{SO}_4^{=}$ artifact. In addition, this method also may overestimate the condensable organic fraction. Because dilution samplers provide conditions that simulate true atmospheric condensation conditions, as compared to impinger condensation, results obtained by this technique are more representative of the actual PM emissions from gas-fired combustion sources such as this heater. Due to the low filterable PM results, the actual mass collected on the filters was at, or below, the practical limits of the EPA methods as practiced in these tests.

POTENTIAL EMISSIONS MARKER SPECIES

The results obtained using the dilution sampler are believed to provide the best representation of the chemical species present in the stack gas emissions. Ions, carbon, and other elements were detected in both stack and ambient air samples. A comparison of the observed concentrations of these species in ambient and stack samples can provide an indication of which species are considered good markers of natural gas combustion for this source.

Ca, Cl, K, Si, and Ti concentrations are higher in the ambient air sample than for the in-stack sample (Figure 7-3), therefore, it is questionable whether the major source of these species is the combustion process. Cr, Mn, Ni, Rb, Sr, Tl, and Zr were detected in ambient air but not in stack emissions (the detection levels for in-stack samples are approximately 36 times higher than those for ambient air samples). Other species cannot reliably be distinguished because the 95 percent lower confidence bound of the in-stack concentrations is less than the minimum method detection limits (Figure 7-4); these include: Al, Br, Ca, Cd, Cl, Cu, Fe, K, P, Pb, Ti, V, Zn, Cl^- , and EC. Subtraction of the ambient from in-stack concentrations provides an indication of which species can be considered to be emissions markers (Figure 7-5). One standard deviation of the data is indicated by the error bar. Ignoring species found near detection limits, the resulting emissions profile suggests that S, $\text{SO}_4^{=}$, and OC are potential emissions markers.

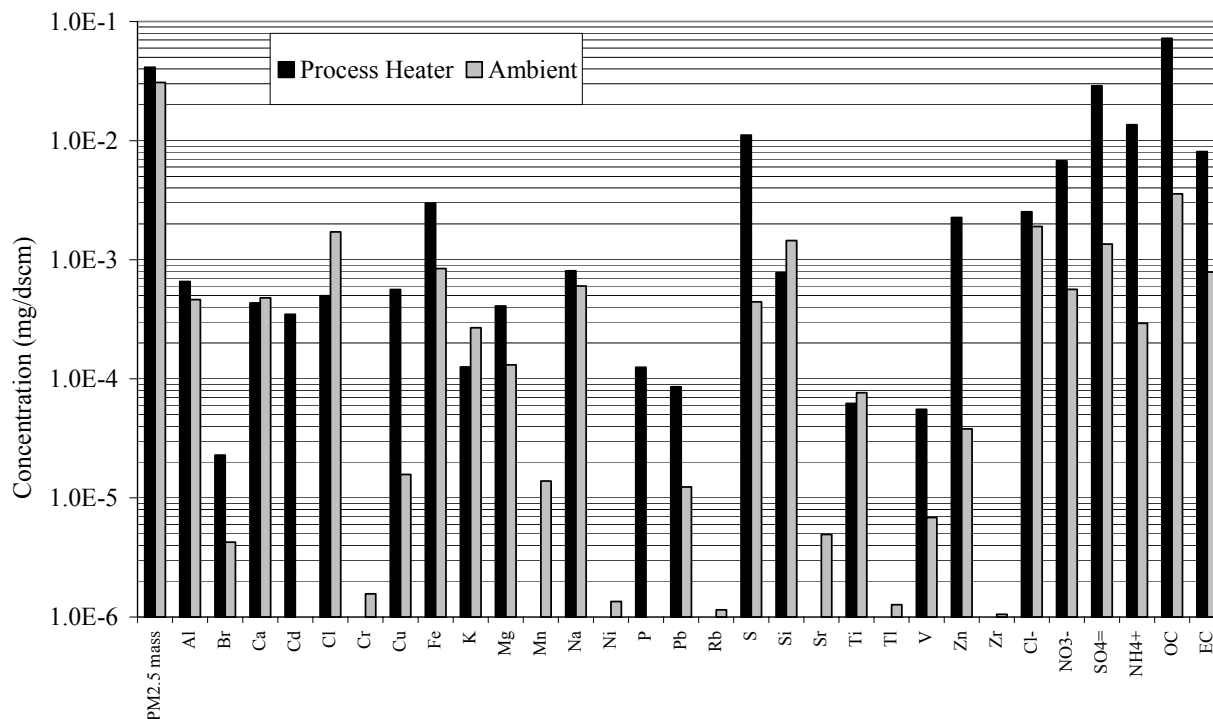


Figure 7-3. Mass Speciation for Dilution Sampler Ambient and Stack Samples (Site Alpha).

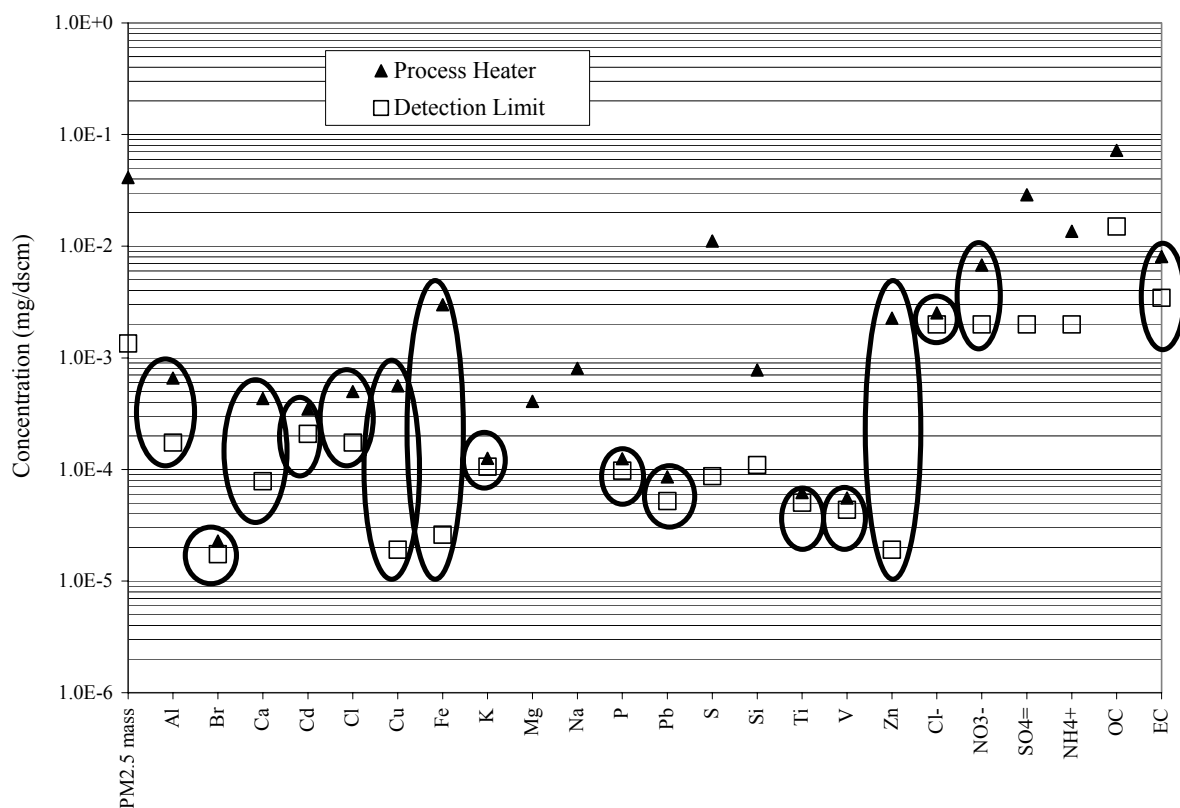


Figure 7-4. Comparison of Average Sample Concentration and Detection Limits (Site Alpha).

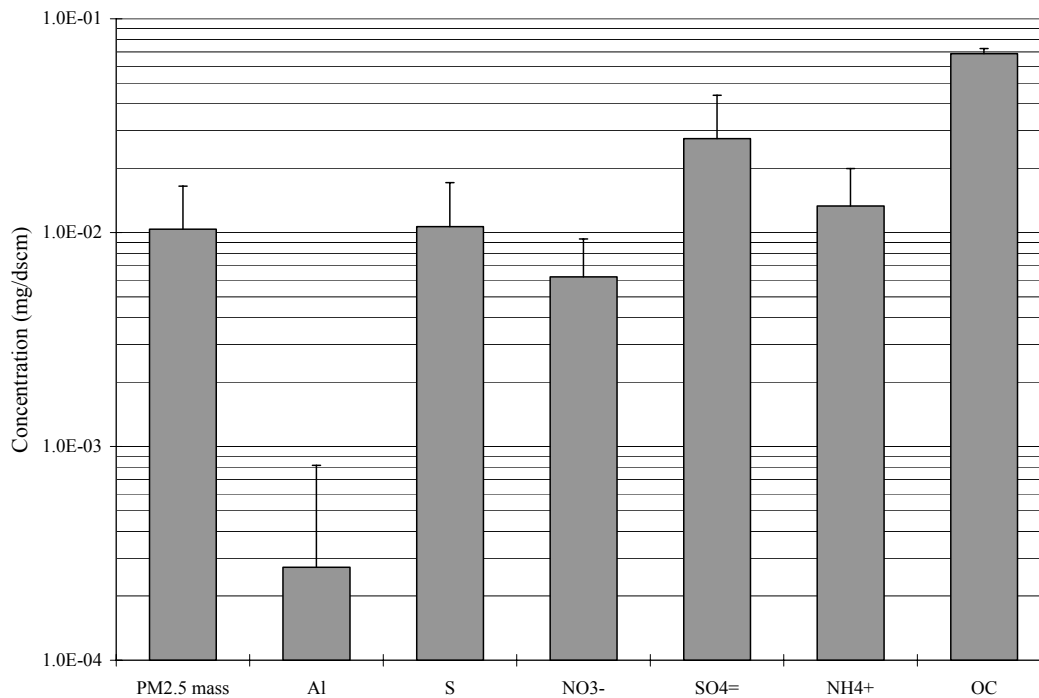


Figure 7-5. Average Sample Concentration Minus Ambient Concentration (Site Alpha).

The uncertainty of several of these values is large, as reflected in the high standard deviations, casting doubt on any of the species being definitively used as an emissions marker. The sum of the ions, elements and carbon species detected on the filters are almost an order of magnitude greater than the PM 2.5 mass. Some of this difference is from the high OC value, which is most likely an artifact, as discussed previously. The ambient concentrations of a majority of the inorganic species are not significantly different from their average sample concentrations. Other compounds were present at lower levels but the low concentrations and high or unknown standard deviations associated with these suggest that they may not be reliable markers.

Organic Speciation Profile

Another potentially useful marker for source emissions is the organic emissions profile. All of the SVOCs detected were present at low concentrations. All SVOCs measured by the dilution sampler, and present at detectable levels, were found at concentrations 10 times greater than ambient levels. Total carbon from SVOCs accounts for approximately 5 percent of the OC measured by the dilution sampler indicating the presence of unspciated organics. This difference stems from the different analytical methods, since the TOR method defines OC

somewhat arbitrarily, as well as by the presence of organics that are not quantifiable by the methods used in this study. In addition, the quartz filter adsorption artifact likely caused the measured OC value to be elevated above actual in-stack OC concentrations.

Organic carbon emissions for Site Alpha were within an order of magnitude of those found at Site B studied earlier in the API/DOE/GRI PM_{2.5} project (Table 7-7), and lower than those from Sites A and C. SVOC emissions at Site Alpha were approximately 8 times higher than those at Site B. VOC emissions from Site Alpha were approximately an order of magnitude lower than those from Site B.

Table 7-7. Average Organic Aerosol Emission Factor Comparison (lb/MMBtu).

Source	Unit Type	Organic Carbon	Elemental Carbon	Total Carbon	Sum of All SVOCs	Sum of All VOCs
Site A	Refinery Gas-fired Boiler	1.5E-4	9.4E-5	2.5E-4	4.1E-6	1.6E-4
Site B	Refinery Gas-fired Process Heater	2.8E-5	1.9E-5	3.4E-5	6.6E-7	4.0E-4
Site C	Natural Gas-fired Steam Generator	2.3E-4	9.2E-6	2.4E-4	1.5E-5	4.1E-5
Site Alpha	Refinery Gas-fired Process Heater	9.3E-5	1.0E-5	1.0E-4	5.5E-6	3.6E-5*

* Does not include VOCs from canister samples.

Elevated levels of organic compounds in the stack samples as compared to levels detected in the blank and the ambient air indicate that potential marker species are more likely to be found within the volatile and semivolatile organic compounds. For Site Alpha, 1,3+1,6+1,7-dimethylnaphthalene, 2-ethyl-1-methylnaphthalene, and acenaphthylene are present at levels significantly above (greater than two standard deviations) their ambient concentrations, and might be potential marker species. However, motor vehicles are also predominant sources of methylnaphthalenes. Because the ambient air was only sampled on one day, it is possible that elevated levels of these compounds were present in the ambient air during source sampling that were not present when the ambient sample was taken. In addition, the relative concentrations of these compounds may not be unique enough to clearly distinguish this source from other external combustion sources.

More comparison to existing speciation profiles is necessary to gauge the uniqueness of the profile produced by this test. In addition, further testing of similar sources is recommended to provide a more robust basis for the emission factors and speciation profiles described herein.

FINDINGS

The main findings of these tests are:

- Particulate mass emissions from the heater were extremely low, consistent with levels expected for gaseous fuel combustion. The low particulate loading associated with gas combustion may contribute to the large uncertainties in the collected mass.
- Two methods for determining the average emission factor for primary PM_{2.5} mass gave results which differed by more than an order of magnitude: 5.2×10^{-5} lb/MMBtu using the dilution sampler; and 8.2×10^{-3} lb/MMBtu using conventional in-stack filters and iced impinger methods for filterable PM (FPM) and CPM, respectively.
- Sampling and analytical artifacts principally caused by gaseous SO₂ in the stack gas were shown to produce a relatively large positive bias in CPM as measured by conventional iced impinger train methods. These measurement artifacts can explain most of the difference between dilution sampling and conventional method results. The results using conventional EPA methods are nominally consistent with published EPA emission factors for external combustion of natural gas (U.S. EPA, 1998). Therefore, the published EPA emission factors derived from tests using similar measurement methods also may be positively biased.
- Chemical species were measured and when summed were approximately four times greater than the measured PM_{2.5} mass, assuming the highest stable oxide forms for metals.
 - Organic and elemental carbon together are almost two times higher than the primary PM_{2.5} mass measured on the Teflon[®]-membrane filter (TMF).
 - The quartz filter used for ion and carbon speciation is subject to organic absorptive bias, especially in low load sources, such as gas-fired heaters, so a likely source of this difference is the high organic carbon value. A backup quartz filter sampled behind the TMF indicated that almost all of the organic carbon might be due to adsorption bias.
- Most elements are not present at levels significantly above the background levels in the ambient air or the minimum detection limits of the test methods to provide representative emission factor data.
- Most organic species are not detected at levels significantly above background levels in the ambient air or field blanks. All detected organics are present at extremely low levels consistent with gaseous fuel combustion.
- Emissions of secondary particle precursors are low and consistent with levels expected for gaseous fuel combustion.

REFERENCES

- ASME. 1998. Test Uncertainty. ANSI/ASME PTC 19.1-1998, American Society of Mechanical Engineers, New York, NY.
- BAAQMD. 1982. *Source Test Procedure ST-1B: Integrated Ammonia Sampling*. Bay Area Air Quality Management District. San Francisco, CA.
<http://www.baaqmd.gov/mop/vol4/v4index.htm>
- Brook, J.R. and T.F. Dann. 1999. Contribution of Nitrate and Carbonaceous Species to PM_{2.5} Observed in Canadian Cities. *Journal of the Air and Waste Management Association*. 49: 193-199.
- Chao, S., K. Crippen, and A. Janos. 1999. Analysis of Trace Level Compounds in Natural Gas. Gas Technology Institute, Final Report, GRI-99/0111.
- Chow, J. and J. Watson. 1998. Guideline to Speciated Particulate Monitoring. Prepared for Office of Air Quality Planning and Standards, U.S EPA. Draft 3, August 1998.
- Corio, L.A. and J. Sherwell. 2000. In-stack condensible particulate matter measurements and issues. *Journal of the Air and Waste Management Association*. 50: 207-218.
- England, G. C., B. Toby, and B. Zielinska. 1998. Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles. Publication No. 344, Health and Environmental Affairs Department, American Petroleum Institute, Washington, D.C.
- England, G.C., B. Zielinska, K. Loos, et al. 2000. Characterizing PM_{2.5} emission profiles for stationary sources: comparison of traditional and dilution sampling techniques. *Fuel Processing Technology*, 65-66, 177-188.
- Filadelfia, E. J. and M. D McDannel. 1996. Evaluation of False Positive Interferences Associated with the Use of EPA Method 202. Air and Waste Management Association 89th Annual Meeting and Exhibition, Nashville, Tennessee, June 1996.
- Grosjean, D., and J.H. Seinfeld (1989). "Parameterization of the formation potential of secondary organic aerosols." *Atmos. Environ.*, 23: 1733-1747.
- Hildemann, L.M., G.R. Cass, and G.R. Markowski. 1989. A dilution stack sampler for organic aerosol emissions: Design, characterization, and field tests. *Aerosol Science and Technology*. 10: pp. 193-204.
- Hildemann, L.M., G.R. Markowski, and G.R. Cass. 1991. Chemical Composition of Emissionfs from Urban Sources of Fine Organic Aerosol. *Environmental Science and Technology*. 25: pp. 744-759.

Hildemann, L. M., D.B. Klinedinst, G.A. Klouda, L.A. Currie and G.R. Cass. 1994. Sources of Urban Contemporary Carbon Aerosol. *Environmental Science & Technology*. 9: 28.

Kirchstetter, T.W., C.E. Corrigan and T. Novakov. 2001. Laboratory and Field Investigation of the Adsorption of Gaseous Compounds onto Quartz Filters. *Atmospheric Environment*. 35: pp. 1663-1671.

Maddalone, R.F., S.F. Newton, R.G. Rhudy, and R.M. Statnick. 1979. *Journal of Air Pollution Control Association*. 29: pp. 626-631.

McDonald, J., B. Zielinska, E. Fujita, J. Chow, J. Watson, J. Sagebiel, T. Hayes, L. Sheetz and S. Batie. 1998. Chemical Speciation of PM_{2.5} Emissions from Residential Wood Combustion and Meat Cooking. Air and Waste Management Association Specialty Conference on PM_{2.5}: A Fine Particulate Standard, Long Beach, CA, January 1998.

McDow, S.R. and J.J. Huntzicker. 1993. Vapor Adsorption Artifact in the Sampling of Organic Aerosol.

Meij, R, 1994. Trace element behavior in coal-fired power plants. *Fuel Processing Technology*. Vol. 39, No. 1/3, pp. 199-214.

SCAQMD. 1990. *Analytical Method for Ammonia and Ammonium Compounds from Stationary Sources by Nessler Colorimetry (Draft Method)*. South Coast Air Quality Management District. Diamond Bar, CA.

Schauer, J.J. and G.R. Cass. 2000. Source Apportionment of Wintertime Gas-Phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers. *Environmental Science and Technology*. 34: pp. 1821-1832.

Turpin, B.J. and J.J. Huntzicker. 1991. Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations. *Atmospheric Environment*. 25A: pp. 207-215.

Turpin, B.J. and J.J. Huntzicker. 1994. Investigation of Organic Aerosol Sampling Artifacts in the Los Angeles Basin. *Atmospheric Environment*. 28: pp. 3061-3071.

Turpin, B.J., P. Saxena and E. Andrews. 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment*. 34: 2983-3013.

U.S. EPA. 1996. *Method 202 – Determination of Condensable Particulate Emissions from Stationary Sources*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. <http://www.epa.gov/ttnemc01/promgate>.

U.S. EPA. 1997. *Method 201A – Determination of PM₁₀ Emissions (Constant Sampling Rate Procedure)*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. <http://www.epa.gov/ttnemc01/promgate>.

U.S. EPA. 1999a. *Particulate Matter (PM_{2.5}) Speciation Guidance Document*. Draft Guidance Document. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. pp. 97-108.

U.S. EPA. 1999b. *EPA Preliminary Method PRE-4 – Draft Method for Determination of PM₁₀/PM_{2.5}*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. <http://www.epa.gov/ttn/emc/prelim.html>

U.S. EPA. 1999c. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. *Compendium Method TO-11A – Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*. U.S. Environmental Protection Agency. Center for Environmental Research Information, Office of Research and Development. Cincinnati, OH.

U.S. EPA. 1999d. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. *Compendium Method TO-13A – Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)*. U.S. Environmental Protection Agency. Center for Environmental Research Information, Office of Research and Development. Cincinnati, OH.

U.S. EPA. 1999e. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. *Compendium Method TO-15 – Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*. U.S. Environmental Protection Agency. Center for Environmental Research Information, Office of Research and Development. Cincinnati, OH.

U. S. EPA. 2000a. Supplement F to the Fifth Edition of AP-42. *Compilation of Air Pollutant Emission Factors Volume I: Stationary Point and Area Sources*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U. S. EPA. 2000b. *Method 17 – Determination of Particulate Matter from Stationary Sources*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. <http://www.epa.gov/ttnemc01/promgate>.

Wien, S.E., G.C. England, K.R. Loos and K. Ritter. 2001. Investigation of Artifacts in Condensable Particulate Measurements for Stationary Combustion Sources. Air and Waste Management Association 94th Annual Meeting and Exhibition, Orlando, Florida, June 2001.

Winegar, E. 1993. Sampling and Analysis of Airborne Pollutants – Chapter 12: Vapor Adsorption Artifact in the Sampling of Organic Aerosol. Lewis Publishers, Inc. pp. 191-208.

Zielinska, B., J. Sagebiel, G. Harshfield, A.W. Gertler and W.R. Pierson. 1996. Volatile Organic Compounds in the C₂-C₂₀ Range Emitted from Motor Vehicles: Measurement Methods. *Atmospheric Environment*. 30: pp. 2269-2286.

Appendix A

LIST OF ABBREVIATIONS

(Na) ₂ SO ₄	sodium sulfate
°C	degrees Celsius
°F	degrees Fahrenheit
µg	micrograms
µg/cm ²	micrograms per square centimeter
µm	micrometers
AC	automated colorimetric system
acfm	actual cubic feet per minute
ACS	American Chemical Society
Ag	silver
Al	aluminum
API	American Petroleum Institute
As	arsenic
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
Au	gold
B	boron
Ba	barium
Be	beryllium
Bph	barrels per hour
Br	bromine
Btu/ft ³	British thermal unit per cubic foot
Ca	calcium
Cd	cadmium
CEC	California Energy Commission
CEMS	continuous emissions monitoring system
cfm	cubic feet per minute
CHON	analysis for carbon, hydrogen, oxygen and nitrogen
Cl ⁻	chloride ion
Cl	chlorine
CO	carbon monoxide
Co	cobalt
CO ₂	carbon dioxide
CPM	condensable particulate matter
Cr	chromium
Cu	copper
DI	distilled deionized
DNPH	dinitrophenylhydrazine
DOE	United States Department of Energy
DRI	Desert Research Institute
dscfm	dry standard cubic feet per minute
dscmm	dry standard cubic meters per minute
EC	elemental carbon

LIST OF ABBREVIATIONS (Continued)

ECD	electron capture detection
ED-XRF	energy dispersive x-ray fluorescence
EI	electron impact
EPA	Environmental Protection Agency
ERA	Environmental Research Associates
eV	electron volts
FCCU	fluidized catalytic cracking unit
Fe	iron
FID	flame ionization detection
FPM	filterable particulate matter
g	grams
Ga	gallium
GC	gas chromatography
GC/IRD/MSD	gas chromatography/infrared detector/mass selective detector
GC/MS	gas chromatography/mass spectrometry
GE EER	General Electric Energy and Environmental Research Corporation
GRI	Gas Research Institute
H ₂ O	water
H ₂ S	hydrogen sulfide
HC	hydrocarbon
HEPA	high efficiency particulate air
Hg	mercury
HHV	higher heating value
HPLC	high performance liquid chromatography
IC	ion chromatography
ICP/MS	inductively coupled plasma/mass spectrometry
In	indium
K	potassium
K ₂ CO ₃	potassium carbonate
keV	kilo electron volts
KHP	potassium hydrogen phthalate
La	lanthanum
lb/hr	pounds per hour
lb/MMBtu	pounds of pollutant per million British thermal units of gas fired
Lpm	liters per minute
MDL	method detection limit
MeCl ₂	methylene chloride
Mg	magnesium
mg	milligram
mg/dscm	milligrams per dry standard cubic meter
MID	multiple ion detection
ml	milliliter
ml/min	milliliters per minute

LIST OF ABBREVIATIONS (Continued)

mm	millimeter
MMBtu	million British thermal units
MMBtu/hr	million British thermal units per hour
Mn	manganese
Mo	molybdenum
MSD	mass selective detector
MSD/FTIR	mass selective detector/Fourier transform infrared detection
n/a	not applicable
N ₂	nitrogen
Na	sodium
Na ⁺	sodium ion
NaCl	sodium chloride
NaNO ₃	sodium nitrate
ND	not detected
ng/μl	nano grams per microliter
NH ₄ ⁺	ammonium ion
NH ₄ OH	ammonium hydroxide
Ni	nickel
NIST	National Institute of Standards and Technology
NMHC	non-methane hydrocarbon
NO ₃ ⁻	nitrate ion
NO _x	oxides of nitrogen
NYSERDA	New York State Energy Research and Development Authority
O ₂	molecular oxygen
OC	organic carbon
P	phosphorus
PAH	polycyclic aromatic hydrocarbon
Pb	lead
Pd	palladium
pH	potential of hydrogen
PM	particulate matter
PM10	particulate with aerodynamic diameter less than 10 micrometers
PM2.5	particulate with aerodynamic diameter less than 2.5 micrometers
ppm	parts per million
ppmv	parts per million (volume)
PUF	polyurethane foam
QA	quality assurance
Rb	rubidium
RSD	relative standard deviation
S	sulfur
Sb	antimony
scfh	standard cubic feet per hour
SCR	selective catalytic reduction

LIST OF ABBREVIATIONS
(Continued)

sdcf	standard dry cubic feet
Se	selenium
Si	silicon
SI	Système Internationale
Sn	tin
SO ₂	sulfur dioxide
SO ₄ ⁼	sulfate ion
Sr	strontium
SRM	standard reference material
SS	stainless steel
SVOC	semivolatile organic compound
Ti	titanium
TIGF	Teflon-impregnated glass fiber
Tl	thallium
TMF	Teflon-membrane filter
TOR	thermal/optical reflectance
U	uranium
V	vanadium
VOC	volatile organic compound
WHRB	waste heat-recovery boiler
XAD-4	Amberlite® sorbent resin (trademark)
XRF	x-ray fluorescence
Y	yttrium
Zn	zinc
Zr	zirconium

Appendix B
SI CONVERSION FACTORS

	<u>English (US) units</u>	X	<u>Factor</u>	=	<u>SI units</u>
Area:	1 ft ²	x	9.29 x 10 ⁻²	=	m ²
	1 in ²	x	6.45	=	cm ²
Flow Rate:	1 gal/min	x	6.31 x 10 ⁻⁵	=	m ³ /s
	1 gal/min	x	6.31 x 10 ⁻²	=	L/s
Length:	1 ft	x	0.3048	=	m
	1 in	x	2.54	=	cm
	1 yd	x	0.9144	=	m
Mass:	1 lb	x	4.54 x 10 ²	=	g
	1 lb	x	0.454	=	kg
	1 gr	x	0.0648	=	g
Volume:	1 ft ³	x	28.3	=	L
	1 ft ³	x	0.0283	=	m ³
	1 gal	x	3.785	=	L
	1 gal	x	3.785 x 10 ⁻³	=	m ³
Temperature	°F-32	x	0.556	=	°C
	°R	x	0.556	=	K
Energy	Btu	x	1055.1	=	Joules
Power	Btu/hr	x	0.29307	=	Watts